Research article

Numerical investigation of flammable vapour cloud formation from pools of heated organic liquids

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A R T I C L E   I N F O

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- Flammable cloud

A B S T R A C T

The aim of this work is to study the effects of wind velocity, pool length and thickness on the flammable vapour cloud formation from pools of heated organic liquids, covering a wide range of substance properties such as molecular weights and boiling temperatures. To achieve that goal, the computational fluid dynamics (CFD) model has been built and implemented in the commercial CFD code ANSYS Fluent. The mathematical model is validated against published experimental data with respect to both pool evaporation and vapour dispersion simulation. The vapour cloud formation is studied in terms of evaporated mass per unit area of the pool, flammable mass of vapours and its fraction of the total released mass, and maximum downwind extent of the flammable cloud. The results of numerical simulation presented in this work provide a better understanding of evaporation and dispersion processes accompanying the formation of a flammable vapour cloud from pools of heated hydrocarbon liquids.

1. Introduction

Petrochemical and oil-refinery industries have been growing rapidly, providing a wide variety of valuable materials and products. However, during the processing, storage, and transportation, large quantities of flammable substances, e.g. hydrocarbons, may be involved. Various factors such as material failure, design deficiency, operation error, or external collision and impact can lead to the vessel or pipeline rupture and release of hazardous material into the environment (Liu et al., 2021). The accidental release of flammable liquids may produce a vapour-air cloud that is capable of being involved in a flash fire or explosion, if ignition source is present. These incidents can lead to severe consequences causing damage to the property and human health. Consequence analysis of possible scenarios is essential in process safety management.

In order to accurately evaluate the hazards of flammable liquid spills, it is necessary to correctly estimate the mass of fuel in the vapour cloud that is within the flammable range (flammable mass) and the extent of the hazardous area. Estimates of flammable mass and the extent of flammable vapour cloud are needed for quantification of fire and explosion hazards as part of a quantitative risk analysis (QRA). QRA typically uses many case scenarios combining consequence estimation with event frequencies (Woodward, 1998). Besides, the flammable vapour cloud characteristics are valuable for determining the detection device distribution and arrangement, use of mitigation systems, and emergency response (Rad et al., 2017; He et al., 2020; Shen et al., 2020; Liu et al., 2021).

To predict the vapour cloud characteristics, the accurate source term and dispersion mathematical models are required. In the past decades, a number of works concerning the modelling and investigation of vapour cloud formation from spills of flammable liquids have been performed. However, some aspects of the phenomenon under study have not been addressed in these works. The deeper understanding of processes that accompany the formation of vapour cloud from flammable liquid spills is important both from a scientific point of view and from the practical perspective of decision-making in process safety engineering.

Since the pool evaporation is a major source of the flammable vapour cloud in case of the release of non-boiling liquids, there is a need to know the evaporation rate of liquids from the pool surface. There are many studies focused on the vaporization of cryogenic liquids (e.g. Gopalaswami et al., 2017; Nawaz et al., 2019; Gao et al., 2020; Nguyen et al., 2020), however, there is a lack of work investigating the vaporization of non-boiling flammable liquids and related hazards. The vaporization of cryogenic liquids is mainly driven by the heat flux from the environment, while the evaporation of non-boiling liquids is driven by the vapour pressure and wind. The following papers...
among recent works relating to the evaporation of volatile non-boiling liquids are worth noting (Heymes et al., 2013; Bubbico and Mazzarotto, 2016; Habib and Schalau, 2019; Pénelon et al., 2020). Heymes et al. (2013) suggested semi-empirical correlation, where constant and exponents are obtained from the fitting of experimental data concerning evaporation from pools of volatile organic compounds and water. Bubbico and Mazzarotto (2016) have tested a number of existing simplified pool evaporation models against the available sets of experimental data, in order to give some guidelines about the ranges of their applicability. Habib and Schalau (2019) have presented results of evaporation open area test site and enclosed space experiments with different liquids vapour pressures of which range up to values close to the boiling point. They have proposed a new model which covers low-wind speed and high-vapour pressure cases. Pénelon et al. (2020) present small- and medium-scale experiments of pool evaporation carried out with liquid hydrocarbons (pentane, heptane), hydrocarbon “gasoline-like” mixtures and gasoline. The authors finally suggest a new semi-empirical correlation with a set of parameters fitted for the performed experiments.

The limitation of the above semi-empirical and semi-analytical models of the pool evaporation assumes the fact that the vapour behaves as a passive contaminant, i.e. it does not affect the flow field above the pool. The mean-velocity profile and the turbulent structure of the airflow may be altered when the evaporating component has a molecular weight different from the one of the environmental air because the buoyancy effects produced by density differences above the pool surface may become important. This leads to a complex coupled problem which requires taking into account the reciprocal influence of the evaporation and dispersion phenomena. Few studies have been conducted to investigate the effect of resulting vapour cloud on the pool evaporation.

Most of these works, for example (Sharpley and Boelter, 1938; Boelter et al., 1946; Sparrow et al., 1983; Bower and Saylor, 2009; Kumar and Arakeri, 2015; Medrado et al., 2021), focused on the evaporation from the water surface under the buoyancy induced by vapour concentration and/or temperature gradients on the air side of the interphase boundary. There is significantly less research addressing the issue of the interaction between evaporation and vapour dispersion for pools of flammable and/or toxic liquids molecular weight of which is greater than that of the ambient air (Galeev and Ponikarov, 2014; He et al., 2017; Galeev et al., 2020).

At refining and petrochemical plants, the liquids are often heated above the ambient temperature. The process of formation of a flammable cloud from a heated liquid pool is highly non-stationary due to liquid cooling in the course of time. The decrease in liquid temperature lowers the vapour pressure and, thereby, reduces the evaporation rate. The simplification of the evaporation rate calculation by assuming constant vapour pressure over time may lead to over-prediction of the consequences and, hence, to overdosing of safety mitigation measures. There is very little research regarding hazards related to accidental spills of heated flammable liquids. To the best of our knowledge there have been no previous studies that examine the combined effects of the pool length, pool thickness, liquid properties and wind velocity on vapour cloud formation from pools of heated flammable liquids. Galeev and Ponikarov (2011) addressed the topic of vapour cloud formation from the pool of heated oil using CFD simulations of evaporation and vapour dispersion processes. In the mentioned work, the effect of the pool depth and wind speed on the evaporation and dispersion characteristics was studied. There is the effect of liquid composition and horizontal pool sizes on the processes accompanying the vapour cloud formation not addressed in the paper. Besides, there no validation of the proposed evaporation model has been done. Beji and Merci (2018) presented a modelling approach of liquid pool evaporation under an external heat flux that is suitable for pool fires.

The above discussion shows that more research is required to improve understanding of the mechanism of vapour cloud formation from pools of heated flammable liquids. The vapour cloud formation from a heated liquid pool is a rather complicated process since it is dependent on numerous variable and changing factors, such as liquid and vapour properties, pool size and thickness, wind velocity and turbulence. In order to capture all important effects related to the evaporation from the pool of heated liquids and resulting vapour dispersion, there is a need to use the CFD tool. The CFD approach can resolve such complex problem through simultaneous calculation of partial differential equations of mass, energy, species, velocity components and turbulence quantities.

The aim of this work is to study the effect of wind velocity, pool length and thickness on flammable vapour cloud formation from pools of heated organic liquids, covering a wide range of liquid properties, such as molecular weights and boiling temperatures. To achieve that goal, the CFD model has been built and implemented in the commercial CFD code ANSYS Fluent version 18.0. User-defined functions (UDFs) are developed to implement the necessary equations for the pool in the CFD code. The proposed approach makes it possible to calculate the evaporation rate from pools with fixed dimensions, taking into account changes in the local liquid mass and temperature. This approach does not require the incorporation of multiphase models, making it beneficial in terms of computational cost. The pool evaporation model is applied in conjunction with the dispersion model in order to take into account the complex interaction between pool evaporation and vapour dispersion processes. The similar approach has already been employed in our previous studies (Galeev and Ponikarov, 2014; Galeev et al., 2013, 2015, 2020), however, the present model has some essential differences from the earlier one: 1) the semi-empirical vertical profiles for mean wind speed and turbulence quantities are specified as the boundary conditions at the inlet to the computational domain instead of profiles from repeated calculations; 2) the turbulence model coefficients are adjusted in order to improve the homogeneity of turbulence quantities and velocity profiles throughout the computational domain; 3) the standard k-ε model is chosen instead of realizable k-ε model in order to be able to adjust the coefficients of the turbulence model in the Fluent; 4) the mole-based formulation for the correction for Stefan flow is used instead of the mass-based formulation; 5) a limiting value of the logarithmic term in the equation for the correction for Stefan flow is proposed to avoid ‚unphysical‘ values of the evaporation rate at liquid temperatures close to the boiling point. The modified mathematical model is validated against published experimental data with respect to both pool evaporation and vapour dispersion simulation.

2. Mathematical model

2.1. Basic equations

The pool is introduced into the CFD code ANSYS Fluent version 18.0 through user-defined scalar (UDS) transport equations without convection and diffusion terms for local liquid mass and temperature. The pool evaporation model is applied in conjunction with the dispersion model. The pool surface is set as a wall boundary and the mass flux \( S_v \) of vapour is introduced to the species transport calculation as a «source term» in the gas-phase cells adjacent to the pool surface. The evaporation rate from the pool surface is determined using Eqs. (1)–(8). The model of vapour dispersion in the atmosphere comprises the system of three-dimensional Reynolds-averaged Navier-Stokes equations, energy and species equations. The governing equations for vapour dispersion are closed using the standard k-ε equations for turbulence. Further details about governing equations of the dispersion model can be found in the CFD code documentation (ANSYS Fluent Theory Guide, 2017), therefore, they are not described in this article. The turbulence model coefficients \( C_{\mu} \) and \( C_{\nu} \) have been modified in order to ensure uniformity of the velocity, turbulent kinetic energy and its dissipation rate profiles for the wind flow along the computational domain. The justification for the choice of these coefficient values will be discussed later in Section 2.2. To ensure that the model provides reliable results in simulation of evaporation and vapour dispersion, its validation is performed in Sections 2.3 and 2.4.
When developing the pool evaporation model the following assumptions were made:

- the pool formation process is not taken into account;
- the liquid is assumed to be ideally mixed across a liquid layer height;
- the free boundary of the liquid during evaporation is motionless;
- the vapour at the interface is saturated

The evaporation rate \( J_{e,v} \) from the pool surface is calculated using the standard wall functions (ANSYS Fluent Theory Guide, 2017) and taking into account the correction for Stefan flow:

\[
J_{e,v} = K \left( Y_{v} - Y_{v,p} \right) \frac{\rho C_{p}^{2.5} K_{p}}{\mu} ; \\
Y^{+} = \begin{cases} \mathcal{S}_{c} \cdot \frac{y^{+}}{C_{v}} & (y^{+} \leq y_{c}^{+}) \\ \mathcal{S}_{c} (u^{+} + P_{C}) & (y^{+} > y_{c}^{+}) \end{cases} \\
= \frac{\rho C_{p}^{2.5} K_{p} y^{+}}{\mu} ; \\
u^{+} = \frac{1}{K} \ln \left( E y^{+} \right) - \Delta B; \\
\Delta B = \begin{cases} 0 & (K_{P}^{+} \leq 2.25) \\ \frac{1}{2} \ln \left( \frac{K_{P}^{+} - 2.25}{5.775} + C_{v} \cdot K_{P}^{+} \right) \cdot \sin \left( 0.4258 \cdot \left( \ln K_{P}^{+} - 0.8111 \right) \right) & (2.25 < K_{P}^{+} \leq 90) \\ \frac{1}{2} \ln \left( 1 + C_{v} \cdot K_{P}^{+} \right) & (K_{P}^{+} > 90) \end{cases}
\]

Finally, the turbulent Schmidt number \( \mathcal{S}_{c} \) in pool evaporation and vapour dispersion equations was set equal to a default value of 0.7. It is assumed that the transition between the fully turbulent region and the viscous layer near the pool surface occurs at a value \( y_{c}^{+} \) of 11.

Eq. (8) for correction for Stefan flow is derived from the assumption that the total molar concentration is constant. This is a reasonable assumption in isothermal systems with constant pressure (Çengel and Ghajar, 2015; Sikanen, 2017). In the literature on spray evaporation, the expression for the correction for Stefan flow is often formulated in terms of mass fractions instead of volume fractions (Sazhin, 2017). As mentioned above, the mass-based formulation was also used to describe evaporation from pools in our previous works. This formulation is obtained using the assumption that the total density of the gas mixture does not depend on the distance from the pool surface (Çengel and Ghajar, 2015; Sikanen, 2017). As pointed by Sazhin (2017), this assumption can be incorrect for strongly evaporating droplets with a high surface temperature. The present study examines the heated organic liquids vapours of which have molecular weight higher than that of the ambient air. The evaporation from pools of these liquids can cause the substantial density vertical gradient above the interphase boundary. According to this reasoning, in the present paper the mole-based formulation is chosen for taking the Stefan flow into account. To assess the applicability of the chosen formulation, the model predictions in comparison with the experimental data are presented in Section 2.4. The calculations of evaporation rate using the mass-based formulation are also presented in Section 2.4 for comparison purposes.

It is assumed that the vapour at the interphase boundary is saturated at the local liquid temperature \( T_{lq} \) and, hence, its mole fraction \( X_{v,i} \) at the pool surface is determined as \( X_{v,i} = P_{v}(T_{lq})/P_{o} \). In order to avoid the «unphysical» values of evaporation rate at temperatures \( T_{lq} \) close to the boiling point (at \( T_{lq} = T_{b} \) the logarithmic term in Eq. (8) is equal to infinity), the limiting value of the numerator in Eq. (8) is introduced based on the considerations presented below.

The numerator in Eq. (8) is termed as a rate factor \( \varphi \) by Bird et al. (1960) and it is derived from the film theory. The plot of \( \varphi \) versus \( R = (X_{v,i} - X_{v,P})/(1 - X_{v,i}) \) and \( Sc \) that is derived from the boundary layer theory is also presented by Bird et al. (1960). The limiting value of the rate factor is extracted from the above plot. This value is approximately equal to 2.5 at \( R = 100 \) (approximately corresponds to \( X_{v,i} = 0.99 \), which is very close to the mole fraction of the vapour at the interphase boundary at the boiling point \( X_{v,b}(T_{b}) = 1 \)) and at \( Sc = 2 \) (the molecular Schmidt numbers for organic liquids examined in the present work are close to this value). Finally, the rate factor \( \varphi \), i.e. the numerator in Eq. (8), is determined as:

\[
\varphi = \max \left\{ 2.5; \ln \left[ \frac{(1 - X_{v,P})}{(1 - X_{v,i})} \right] \right\}.
\]

The change in the local pool temperature with time is calculated as follows:

\[
\frac{dT_{lq}}{dt} = \frac{q_{v} + q_{ard} + q_{sol} - q_{w} - \Delta H \cdot S_{r}}{\sum m_{lq} \cdot C_{p,liq}}
\]

where \( q_{v} \) is the convective heat flux, W/m²; \( q_{ard} \) is the heat flux at the liquid-ground interface, W/m²; \( q_{sol} \) is the heat flux from the sun, W/m²; \( q_{w} \) is the long-wave radiation flux emitted by the pool, W/m²; \( \Delta H \) is the long-wave radiation flux from the atmosphere absorbed by the pool, W/m².

The rate of change in the mass of the liquid is given by:

\[
\frac{dm_{lq}}{dt} = -S_{e,v}
\]

where source term \( S_{e} = J_{e,v}/V \); \( V \) is the volume of the cell adjacent to the pool surface.

Besides that, the «source term» \( S_{e} \) is included into the species transport equation, the source term \( S_{h} \) is introduced to the heat transport equation in the cells adjacent to the pool surface:

\[
S_{h} = S_{v} \cdot h_{v}
\]

where sensible enthalpy for vapour \( h_{v} \) is defined as (ANSYS Fluent Theory Guide, 2017):

\[
h_{v} = \int_{T_{ref}}^{T} C_{p,v} \cdot dT
\]

where \( T_{ref} \) is equal to 298.15 K and \( T = T_{lq} \).

The present model takes into account the change in thermophysical properties of liquids and vapours with temperature. The equations for calculating temperature-dependent properties (vapour pressure, latent heat and heat capacity) of several liquids considered in this study, as well as the equations for calculating temperature-dependent properties (heat capacity, thermal conductivity and viscosities) of vapours and air are provided in Appendix A. In general, the calculations from the equations given in Appendix A show that the specific heat of liquid vapours considered in this study (benzene, toluene, ethylbenzene and cumene) increases linearly with temperature – within the temperature range from \( T_{ref} \) to \( T_{b} \). In this case, the definite integral (13) is calculated as follows:

\[
h_{v} = 0.5 \left( T_{lq} - T_{ref} \right) (C_{b,v}(T_{b}) + C_{b,v}(T_{ref}))
\]

Eqs. (1)–(14) are implemented in the CFD code through UDFs.

In the present work, a transient three-dimensional heat transfer equation was solved inside the ground layer to obtain the heat flux from the pool to the ground \( q_{gld} = \varphi_{gld} (\partial T_{gld}/\partial y)_{y=0} \):

\[
C_{P,gld} \rho_{gld} \frac{dT_{gld}}{dt} = \lambda_{gld} \left( \frac{\partial^{2} T_{gld}}{\partial x^{2}} + \frac{\partial^{2} T_{gld}}{\partial y^{2}} + \frac{\partial^{2} T_{gld}}{\partial z^{2}} \right).
\]
The computational domain under fluid domain was constructed to mimic the ground layer. The boundary conditions for Eq. (15) are set as follows: on the surface adjacent to the pool \( T_{y/a}(x,0,z) = T_{liq} \) at the bottom and side boundaries of the underlying layer \( \partial T_{y/a}/\partial n = 0 \), where \( n \) is the normal to the boundary.

The density of the vapour-air mixture is calculated using the incompressible ideal gas law according to Eq. (16). The physical properties of vapour-air mixture are computed based on a simple mass fraction average of the properties of pure species (mass-weighted-mixing-law).

The density of the vapour-gas mixture was determined as follows (ANSYS Fluent Theory Guide, 2017):

\[
\rho = \frac{P_0}{RT} \left( \frac{Y_v}{M_v} + \left(1 - \frac{Y_v}{M_v}\right) \frac{M_a}{M_v} \right).
\]  

(16)

2.2. Boundary conditions for the wind flow

Before the transient simulation of pool evaporation and vapour dispersion, we need to determine a steady-state flow field. To calculate the wind flow, the semi-empirical profiles for wind velocity, turbulence kinetic energy and its dissipation rate are set on the inlet boundary of the computational domain instead of the profiles from the repeated calculations (Galeev et al., 2013). In the latter approach, the resulting profiles at the outlet of the domain are applied at the inlet of the same domain; and this procedure with subsequent calculation had been repeated until the profiles at outlet and inlet boundaries became similar. The drawback of this approach is the fact that we need to know initial approximations of wind speed and turbulence quantities to set them on the inlet boundary and to carry multiple runs before the fully-developed profiles of wind speed and turbulence quantities are obtained. The semi-empirical correlations are easier to use, since they do not require the initial value of wind speed to provide the required reference velocity at the respective reference height. However, this approach requires the horizontal homogeneity of wind speed and turbulence throughout the computational domain, i.e. the vertical profiles of mean wind speed and turbulence quantities applied at the inlet boundary should be maintained along the entire length of the computational domain.

The horizontal homogeneity can only be obtained if the inlet profiles of mean wind speed and turbulence quantities are consistent with the turbulence model (including its constants), wall functions and roughness modification (Blocken et al., 2007). In the present work, in contrast to our earlier ones, the standard k-ε turbulence model instead of the realizable k-ε model is utilized to describe the turbulence effects. The choice in favour of the standard k-ε model is made because there is an ability to modify the coefficients of turbulence model \( C_k \) and \( C_{\epsilon} \), using the Fluent program interface to ensure uniformity of the profiles along the length of the domain. There is no opportunity to adjust the above coefficients when using the realizable k-ε model.

In the present study, the neutral atmospheric stratification is considered, therefore, the appropriate profiles and remediation measures are chosen to provide horizontal homogeneity under this condition.

The variation of the wind velocity for neutral stratification is defined by (Bakum and Dujm, 1997):

\[
U(y) = \frac{u_*}{k} \ln \left( \frac{y}{y_0} \right).
\]  

(17)

The expressions for the turbulent kinetic energy \( (k) \) and turbulence dissipation rate \( (\epsilon) \) for neutral and stable atmospheric boundary layers follow the derivation by Han et al. (2000):

\[
k(y) = \begin{cases} 6u_*^2 & \text{for } y \leq 0.1h_{abl} \\ 6u_*^2 \left(1 - y/h_{abl}\right)^{1.75} & \text{for } y > 0.1h_{abl} \end{cases}
\]  

(18)

\[
\epsilon(y) = \begin{cases} \frac{\alpha_s^4}{\epsilon_s} \left(1.24 + 4.3 \frac{y}{h_{abl}}\right) & \text{for } y \leq 0.1h_{abl} \\ \frac{\alpha_s^4}{\epsilon_s} \left(1.24 + 4.3 \frac{y}{h_{abl}}\right) \left(1 - 0.85 \frac{y}{h_{abl}}\right) & \text{for } y > 0.1h_{abl} \end{cases}
\]  

(19)

where \( h_{abl} \) is the height of the atmospheric boundary layer. For neutral boundary layer, the boundary layer height is a function of the friction velocity \( u_* \) and the Coriolis parameter \( f_c \):

\[
h_{abl}\text{neutral} = 0.3 \frac{u_*}{f_c}. \tag{20}
\]

where \( f_c = 0.0001191 \) is the Coriolis parameter.

For neutrally stratified boundary layer the Monin-Obukhov length \( L \rightarrow \infty \).

Eqs. (17)–(20) are implemented in the CFD code through UDFs.

The same expressions (18) and (19) for \( k \) and \( \epsilon \) are also set as boundary conditions for the wind flow in the CFD model FLACS (FLACS-CFD v20. 1 User’s Manual, 2020). However, this model uses the values of coefficients of the original turbulence model proposed by Launder and Spalding (1974), namely \( C_k = 0.09 \) and \( C_{\epsilon} = 1.44 \), whereas in the present model these coefficients are modified to ensure that the vertical profiles of mean wind speed and turbulence quantities are maintained with downstream distance. The coefficient \( C_k \) was set to be equal to 0.0278. This value is obtained by combining equation \( u_* = C_k \cdot k^{1/2} \sqrt{\epsilon} \) and Eq. (18). The coefficient \( C_{\epsilon1} \) is obtained from the expression (Aliot and Masson, 2005):

\[
C_{\epsilon1} = C_{\epsilon2} - \frac{k^2}{\sqrt{C_k \cdot \epsilon}} = 1.114,
\]

where \( C_{\epsilon2} = 1.92 \) is the coefficient of the turbulence model.

A schematic of the computational domain is shown in Fig. 1. At the inlet of the domain (ABCD) the vertical profiles of \( U, k \) and \( \epsilon \) are imposed according to Eqs. (17)–(19). At the outlet boundary (EFGH) the static pressure is imposed to be equal to the ambient pressure (101,325 Pa). Two sides and top of the domain (ABFE, BCGF and DCGH planes) are defined as impermeable symmetry boundaries. At these boundaries, the normal velocity gradients were taken to be zero. The bottom boundary (ADHE) was set as no-slip wall. The x-z plane was placed on the ground and the x-direction is parallel to the wind. To simulate the ground conduction, the solid layer under fluid domain with the height of 2 m is also constructed. When the ground layer is included into the simulation, the coupled boundary condition is set on the wall between the fluid and solid domains. In this case, the conjugate heat transfer problem is solved, when the heat transfer process involves an interaction of conduction within a solid body and the convection from the solid surface to fluid moving over the solid surface. When the wall is defined as a «coupled» boundary, its temperature should satisfy the following condition:

\[
-h_f (T_m - T_P) = \lambda_{abl} \frac{\partial T_{ssl}}{\partial y}, \tag{21}
\]

where \( h_f \) is the heat-transfer coefficient, W/(m²·K)

In Eq. (21), the heat-transfer coefficient is computed on the basis of wall functions (ANSYS Fluent Theory Guide, 2017).

The PRESTO! interpolation scheme was chosen for the spatial discretization of pressure. The SIMPLE algorithm was chosen for pressure-velocity coupling. The second-order upwind scheme was used for the spatial discretization of velocity components, turbulence quantities and species, while the first-order scheme was used for user-defined scalars. The Green-Gauss Node-Based method was used for the computation of gradients.

In Fluent, it is necessary to set the equivalent sand-grain roughness height \( K_z \) for ground surface. In order to provide correspondence of a simulated profile for wind velocity with Eq. (17), Blocken et al. (2007) propose a relationship between \( K_z \) and \( y_0 \):

\[
K_z = 9.793 \cdot y_0 / C_f, \tag{22}
\]

The maintenance of the flow profiles along a domain length should be demonstrated. For this purpose, the simulations of wind flows with reference velocities of 1, 2.5 and 5 m/s at the reference height of 10 m are performed. The structured non-uniform mesh consisting of 433,000
The dispersion of vapour in the atmosphere is significantly influenced by wind speed and turbulent viscosity (turbulent diffusivity), therefore, it is important above all to ensure horizontal homogeneity of these quantities. The maintenance of the velocity and turbulent viscosity profiles were found to be good: the maximum deviation between inlet and outlet values for \( U \) is 5\%, while that for \( \mu_t \) is 10\% up to a height of 50 m.

### 2.3. Validation of the dispersion model

The gas dispersion model is validated against the experimental data sets included in the model evaluation protocol (MEP) database (Ivings et al., 2013). The field data (Maplin Sands, Coyote, Burro) on liquefied natural gas (LNG) vapour dispersion was chosen. An LNG vapour cloud is initially very cold (the boiling temperature of LNG is approximately 111.7 K) and dense (the density of methane vapour at boiling temperature is approximately 1.5 times higher than the density of air at ambient temperature). The experiments under neutral stratification were chosen because the stable and unstable conditions are beyond the scope of the present paper. The spill parameters and meteorological data for experiments are summarized in Table 1.

In the selected experiments, the LNG was spilled onto the surface of the sea (Maplin Sands) or onto the surface of a water pond (Coyote, Burro). Because LNG evaporates very quickly from the water surface area due to the heat transfer between LNG and water, this study, therefore, uses the total vaporization rate equal to the spill rate. In the simulation, the source is represented as a pool and its area is determined by dividing the spill rate by the vaporization rate. It is assumed that the vaporization rate per unit area is equal to 0.085 kg/(m\(^2\)-s) for LNG on water (Hanna et al., 1991). The mass flux \( S_v \) of vapour is introduced to the species transport calculation as a source term in the cells adjacent to the pool surface. The source term for energy is determined by Eq. (13). The thermophysical properties of methane depending on the temperature are calculated using equations given in the handbook (Green and Perry, 2008). In the simulation of selected experiments, the constant temperature at the wall around the pool is specified.

To assess the sensitivity of the solution with respect to the grid refinement, two grids with the total count of cells of 165,000 and 355,000 are used. In the former case, in the spill region, the grid resolution was 1 m\( \times \)0.2 m\( \times \)1 m, whereas in the latter case it was 0.5 m\( \times \)0.1 m\( \times \)0.5 m. The distance from the inlet boundary to the centre of the pool was 520 m. The computational domain sizes were 1500 m in the direction of the wind, 500 m in the crosswind direction and 500 m in the vertical direction. The distance from the inlet boundary to upwind edge of the pool was 500 m. Only half of the pool was considered to save computational resources. Fig. 2 shows the computational grid on the horizontal plane in the pool region.

In the simulations it is assumed that the aerodynamic roughness \( y_0 \) is equal to 0.01 m. According to the user’s manual (ANSYS Fluent Theory Guide, 2017), the sand-grain roughness height \( K_s \) should be less than or equal to the distance \( y_0 \) from the wall (bottom of domain) to the centre point of the wall-adjacent cell. According to Eq. (22) at \( y_0 = 0.01 \) m and at \( C_z = 1 \) (the maximum value which can be set through a user interface), the \( K_s \) is equal to 0.098 m, that is larger than the distance \( y_0 = 0.05 \) m. To meet the requirement \( y_0 \geq K_s \), the roughness height \( K_s \) is set equal to 0.05 m, whereas the value of the coefficient \( C_z \) is set to 1.96 in accordance to Eq. (22). It is not possible to set the value for \( C_z \) higher than 1 via a user interface, therefore, a higher value is defined through a UDF.

The temperature of the ground surface is set equal to the ambient temperature of 303 K.

Figs. 3-5 compare the inlet and outlet profiles for velocity and turbulence quantities (turbulence kinetic energy and its dissipation rate, turbulent viscosity) at reference velocities of 1, 2.5 and 5 m/s at a reference height of 10 m.
2.4. Validation of the pool evaporation model

The pool evaporation model is validated using experimental data obtained by Kawamura and Mackay (1987), Brighton (1990) and Habib and Schalau (2019). Only field experiments were chosen for this purpose. In simulations of these experiments, the thermophysical properties of vapours and liquids depending on the temperature are determined using equations from the handbook (Green and Perry, 2008). For comparison purposes, the evaporation rate calculation was performed using both mole-based and mass-based formulations for the correction factor for Stefan flow.

Among all tests by Kawamura and Mackay (1987), the ones that included the effects of conduction from the ground and heat inflow from the sun, namely tests 18, 19, 20, 21 and 22, were selected. In those experiments, a pan 0.46 m in diameter with a height of 0.102 m was employed. The chemicals tested were n-pentane, toluene, cyclohexane and n-hexane. The evaporation pan was initially filled to a depth of 0.05 m with sand and was subsequently partially buried in the ground, so that the surface of sand was just slightly higher than the ground level. The pan was then filled with the chemical tested and allowed to evaporate in the presence of the wind and the sun. The test was carried out until either the level of chemical remaining in the pan was less than 0.01 m or the experimental duration became excessively long. The evaporation rate was determined by measuring the volume of the chemical remaining in the pan after the termination of the experiment. The conditions of five selected tests are given in Table 2. The wind velocities are not specified in the paper (Kawamura and Mackay, 1987), therefore, these values are obtained using evaporation rate data and two evaporation models by Kawamura and Mackay (1987), as it was done by Fernandez (2013).

A structured grid consisting of 165,000 cells is applied. In the pool region, the minimum grid size was 0.1 m in the horizontal and lateral directions. The height of wall-adjacent cells on the gas side was 0.1 m. The distance from the inlet boundary to the pool centre was
The observed and predicted averaged evaporation rates are reported in Table 3. A good agreement between predicted and measured data is observed at low and moderate wind speeds (tests 18, 19 and 20), whereas at high wind speeds for a highly volatile chemical (n-pentane) the model is found to substantially over-predict the evaporation rate. Table 3 shows that for high-volatile liquids (hexane and n-pentane) the model with the mole-based formulation for correction for Stefan flow $K$ provides a better agreement with the experiment compared to the model with the mass-based formulation for $K$. It is worth noting that for low-volatile liquids (toluene, cyclohexane) the difference between evaporation rates obtained using the mass-based and mole-based formulations is smaller compared to high-volatile liquids (hexane, n-pentane), because in the former case, the both formulations give close values of $K$.

Also, the experiments on evaporation of liquefied n-butane at temperatures below its boiling point were used to validate the pool evaporation model (Brighton, 1990). These experiments were used to validate the model in our earlier work as well (Galeev et al., 2013). In this work, when modelling experiments, the roughness height of the sur-
Fig. 5. Profiles of velocity $U$, turbulence kinetic energy $k$, turbulence dissipation rate $\varepsilon$ and turbulent viscosity $\mu_t$ at reference velocity of 5 m/s at a height of 10 m at the inlet and outlet planes of the computational domain.

| Test no. | Chemical  | Evaporation rate (gm$^{-2}$ s$^{-1}$) | % (mole-based) | % (mass-based) |
|----------|-----------|--------------------------------------|----------------|----------------|
|          |           | Exp. | Calc. (mole-based) | Calc. (mass-based) |           |           |
| 18       | toluene   | 1.08 | 0.98               | 1.02            | 9.6          | 5.9        |
| 19       | cyclohexane | 2.6  | 2.5                | 2.6             | 5.4          | 1.4        |
| 20       | hexane    | 2.0  | 2.2                | 2.4             | 7.6          | 19.2       |
| 21       | n-pentane | 6.39 | 8.1               | 8.9             | 26.3         | 39.2       |
| 22       | n-pentane | 7.53 | 10.5              | 11.5            | 39.6         | 53.0       |

Table 3: Experimental results and model predictions (kg/m$^2$.s).

face around the pool $y_0$ was the same as that for the pool surface, i.e. $y_0 = 0.00022$ m, whereas in the present study a refined calculation of evaporation was carried out taking into account the dependence of roughness of the land upwind the pool on the wind direction. As pointed in the paper (Brighton, 1990) for wind directions 180° and >266° the land upwind the pool was undulating rough side; for directions within the range 186°–266° the surface upwind was very flat for about 80 m (concrete surface). In simulation, in the former case (tests 2, 3, 4, 6, 8), the roughness of the surface around the pool $y_0$ is set equal to 0.01 m, while in the latter case (tests 1, 5 and 7), the flat surface with the roughness height of $y_0 = 0.0002$ m around the pool is created. The relative location of the flat area and pool surface in simulation of the latter case is shown in Fig. 8.

Table 4 shows that the model with mole-based formulation for coefficient $K$ produces a better agreement with experiment than the model with mass-based formulation for $K$. In the latter case, there is a tendency for the model to overestimate the evaporation rate.

Also, to validate the pool evaporation model, the experimental data on evaporation of ethanol and acetone obtained by Habib and Schallau (2019) was used. In these experiments, the basins with diameter of 0.74 m (for ethanol) and with diameter of 0.88 (for acetone) were employed. The pool was heated and the constant liquid temperature was maintained. During experiments with ethanol, the vapour pressure was up to 0.3 bar (abs.), whereas in the experiments with acetone the vapour pressure of 0.94 bar (abs.) was reached. To represent the plots of evaporation rate against air velocity among experiments with ethanol, the ones where pool temperatures are close and wind speeds are different have been selected. For experiments with acetone, it is not possible to provide similar plots due to the significant differences between the pool temperatures.

The computational grid was the same as the one applied in the simulation of Kawamura and Mackay’s tests. The roughness height $y_0$ of the surface around the pool was assumed to be equal to 0.005 m which corresponds to the type of “bare soil” terrain (Troen and Petersen, 1989).

Test conditions with ethanol and acetone are summarized in Appendix B in Tables B1 and B2 respectively. Fig. 9 and Fig. 10 compare the predicted and experimental evaporation rate of ethanol and acetone respectively.

Fig. 9 shows that for all selected tests the models overestimate the evaporation rate of ethanol. The discrepancies between predictions and experimental data increase with wind velocity. The models with mass-based and mole-based formulation for correction for Stefan flow predict very close values of evaporation rates due to the relatively low vapour pressure of ethanol at liquid temperatures during the tests. As shown earlier, a similar result is obtained for low-volatile liquids in simulation of Kawamura and Mackay’s tests. The difference in evaporation rates between simulation and experiment for ethanol ranges from 53 to 220% (for the model with mole-based formulation).

For acetone pool cases, the calculated results agree well with experimental data at low and moderate wind speeds (approximately less than 6 m/s), while at high wind speeds, as in the case of ethanol, the model
Fig. 6. Comparison between simulated peak gas concentrations obtained using coarse and fine grids for field tests (Maplin Sands, Coyote, Burro).

Table 4. Experimental data (Brighton, 1990) and computational results for evaporation rate.

| Test No. | Ambient temperature (K) | Wind speed at height of 9.15 m (m/s) | Pool temperature (K) | Wind direction (magnetic degrees) | Evaporation rate (gm⁻² s⁻¹) |
|----------|-------------------------|--------------------------------------|----------------------|-----------------------------------|-----------------------------|
|          |                         |                                      |                      | Exp. (mass-based)                 | Calc. (mass-based)          | Calc. (mole-based)          |
| 1        | 283                     | 3.5                                  | 236.6                | 200                               | 3.7                         | 4.5                         | 4.08                        |
| 2        | 282                     | 3.0                                  | 241.1                | 155                               | 2.7                         | 4.9                         | 4.39                        |
| 3        | 280                     | 1.5                                  | 244.2                | 305                               | 2.3                         | 2.7                         | 2.41                        |
| 4        | 291                     | 2.4                                  | 241.1                | 61                                | 3.9                         | 3.6                         | 3.28                        |
| 5        | 289                     | 4.8                                  | 236.3                | 255                               | 5.5                         | 6.0                         | 5.52                        |
| 6        | 275                     | 5.5                                  | 238.8                | 279                               | 5.6                         | 8.6                         | 7.81                        |
| 7        | 287                     | 6.9                                  | 236                  | 254                               | 7.2                         | 8.7                         | 8.05                        |
| 8        | 282                     | 1.0                                  | 263                  | 281                               | 2.0                         | 4.5                         | 3.71                        |
with both mole-based and mass-based formulations for correction for Stefan flow strongly over-predicts the evaporation rate. For acetone, the differences between predicted evaporation rates from these models are more significant than for ethanol due to the higher volatility of liquid. As mentioned above, both models provide an acceptable level of discrepancy with the experiment at low and moderate wind speeds, however, in general, in these conditions the model with mole-based formulation tends to under-predict the evaporation rate, while the model with mass-based formulation tends to over-predict it. For acetone at wind speeds less than 6 m/s, the difference between simulation results and experimental data does not exceed 23%, while at wind speeds over 6 m/s it ranges from 42 to 117% (for the model with mole-based formulation).

The reason for the large discrepancy between the simulation results and experimental values of Habib and Schalau (2019) at higher wind speeds may be attributed to the fact that in experiments the pan with liquid was located at a certain height above the ground due to presence of the balance and the raised support under the pan, that may distort the wind profile above the liquid surface.

3. Results and discussion

This section presents and discusses the simulation results for a series of hypothetical case studies obtained using the proposed CFD model. The case studies are pools of heated aromatic liquids, namely, of benzene, toluene, ethylbenzene, and isopropylbenzene (cumene). The sensitivity of evaporation and vapour cloud characteristics to wind velocity, pool length and pool thickness has been assessed. For the sake of convenience, benzene and toluene will be also referred to as «low-boiling liquids», whereas ethylbenzene and cumene – to as «high-boiling liquids». As will be shown below, the substances within the one group («low-boiling liquids» or «high boiling liquids») demonstrate similar behaviour in terms of evaporation and vapour dispersion, but have strong differences from the substances of other group in these aspects.

3.1. Selected substances and scenarios

The selection for simulations of aromatic liquids such as benzene, toluene, ethylbenzene and cumene allows to cover a wide range of properties particularly in terms of molecular weights (from 78.11 to 120.19 kg/kmol) and boiling temperatures (from 80.09 to 152.41 °C).

The computational grid is the same as the one used to check the maintenance of wind velocity and turbulence quantities profiles along the computational domain in Section 2.2. The ground layer under the fluid domain with a height of 2 m and with the same downwind and crosswind dimensions as fluid domain is also included into the simulation to take heat transfer between the ground, pool and gas phase into account. The «coupled» boundary condition is set on the wall between fluid and solid domains outside the pool. The temperature of the wall under the pool is set to be equal to the liquid temperature. The convergence criterion for species transport equation is $1 \times 10^{-5}$, for energy equation and local liquid mass equations is $1 \times 10^{-6}$ and for other variables is $1 \times 10^{-3}$. The maximum time step of 1 s is used.

For all substances, the initial temperature of the liquid is set equal to the boiling temperature $T_b$ at the atmospheric pressure. The initial ground temperature is set equal to the ambient temperature of 303 K. The duration of evaporation from the pool surface is taken to be equal to 3600 s. The square-shaped pools are considered with sizes of 20, 30, 40 and 60 m and with initial depths of 0.01 m and 0.05 m. The reference wind speeds of 1 m/s and 2.5 m/s at a height of 10 m and neutral atmospheric stratification are chosen for simulations. The choice of low wind velocities is made for two reasons: firstly, low wind conditions lead to formation of the most extended flammable clouds, secondly, at higher wind speeds a complete evaporation can be observed in some parts of pools, whereas it is important that the size of pools remains constant throughout the considered period of time in order to correctly compare results for substances being examined with each other.

In simulations of hypothetical large-scale pool cases, the grid size in horizontal directions in the pool area was much larger than that used in the validation of the pool evaporation model (0.5 m versus 0.1 m), whereas the same vertical size of cells adjacent to pool surface was used (0.1 m) both in the validation study and in simulations of hypothetical pool cases. In order to ensure that the grid is appropriate for modelling the evaporation of large-scale pools, the grid sensitivity study for one of the large-scale pool cases (20 m×20 m benzene thicker pool at a wind speed of 1 m/s) was performed. It was found that the reduction in the horizontal dimensions of cells by a factor of two changes the predictions of evaporated mass per unit area by no more than 1.5%.

The ground roughness length $K_z$ was set to 0.098 m (it corresponds to the aerodynamic roughness height $y_0$ of 0.01 m). The pool upwind edge was set to 500 m from the velocity inlet boundary. The thermal conductivity, specific heat capacity and density of the underlying solid layer were set to 1.28 W/(m-K), 1130 J/kg and 2300 kg/m$^3$, to replicate the thermal properties of concrete. The heat flux from the sun to the pool was set to zero.

The thermophysical properties of selected substances depending on the temperature are determined using equations from Green and Perry’s (2008) handbook. These equations and their coefficients are given in Appendix A. The flammable properties of substances are also given in the same annex.

3.2. Simulation results

Figs. 11 (a - d) and 12 (a - d) show the variations of the evaporated mass per unit area $m_{evap}$ and liquid temperature $T_{liq}$ averaged over the entire surface area with time at reference velocities of 1 m/s.
and 2.5 m/s respectively. The plots show that the pool size has considerable influence on the evaporated mass per unit area, especially for low-boiling liquids at a lower wind speed. With the exception of a thicker pool of cumene at a wind speed of 1 m/s, in other conditions being equal, the evaporated mass per unit area is lower when the pool size is larger (the explanation of the specific behaviour of cumene will be discussed later). Generally, the effect of pool size on the evaporation rate decreases with the increase of the wind velocity and decrease of the initial pool depth. The similar effect also was predicted using CFD for non-heated liquid such as hexane (Galeev et al., 2015), where the initial liquid temperature was equal to the temperature of ambient air. In this paper, it is shown that a decrease in the evaporation rate with an increase in pool size largely occurs because of an enhancement of the concentration-induced negative buoyancy of the air-vapour cloud. As the pool size increases, the average vapour concentration above the pool surface and, thus, the air-vapour cloud density increase. The negative vertical density gradient that occurs above the pool surface suppresses the turbulence inside the cloud (stable density stratification) resulting in a large resistance to the transport of vapour away from the evaporating pool, thereby reducing the evaporation rate. Furthermore, an increase in the vapour concentration above the pool surface with the increase of pool length leads to the reduction of the driving force of the mass transfer process. Thus, it can be concluded that for heated liquids the effect of the concentration-induced buoyancy on the pool evaporation remains important, despite the opposite effect of thermal expansion due to the high temperature of the vapour-air mixture at the pool surface and, therefore, the effect of the pool size for those liquids at slight winds is as strongly pronounced as during evaporation of unheated volatile liquids.

For low-boiling liquids, the effect of the pool size on $m_{\text{vap}}$ is significant both at large and small initial pool depths at a lower wind speed, indicating a strong increase of vapour-air cloud buoyancy above the pool surface with increase of pool length. Whereas for pools of high-boiling liquids the evaporated mass per unit area $m_{\text{vap}}$ weakly depends on the pool size both at lower and higher wind speeds. In contrast to high-boiling liquids, for low-boiling liquids, at a wind speed of 1 m/s, the difference in the evaporated mass per unit area between pools of different sizes increases throughout the period under consideration at both initial pool thicknesses, since during this period the vapour concentration above larger pools remains high enough to affect the density of the vapour-air mixture. The effect of pool size is less pronounced for high-boiling liquids compared to low-boiling liquids, because in the former case the liquid temperature decreases sharper relative to its initial value, leading to the sharper decrease of vapour pressure and, as a result, to weaker concentration-induced buoyancy of the vapour-air mixture. Additionally, for high-boiling liquids, the temperature of the vapour-air mixture at the pool surface is so high that thermal expansion counteracts the negative buoyancy induced by vapour concentration difference. As mentioned above, with the exception of a thicker pool of cumene at a wind speed of 1 m/s, the evaporated mass decreases as the pool size increases. The evaporation rate of cumene at a thicker initial pool depth and at a lower wind speed slightly increases with the increase of a pool size. The cause of this specific behaviour of cumene relates to the predominance of the positive buoyancy induced by temperature difference over the negative buoyancy induced by vapour concentration difference. In the simulation, the cumene had the highest initial temperature among substances under consideration. Thus, in this case the large difference between temperatures of the vapour-air mixture near the surface and the ambient air induces a convective instability above the pool that increases the turbulence level and, thus, the mass transfer from the pool. As the pool size increases, the temperature of the vapour-air mixture at the pool surface increases, that, in its turn, intensifies the thermally-induced convection.

A decrease in the effect of pool size on the evaporated mass per unit area with a wind speed increase is related to the reduction of the vapour-air mixture buoyancy. The latter happens due to the influence of two factors: firstly, a higher wind speed intensifies mixing of the vapour-air cloud, leading to the alignment of vapour concentration in the vertical direction (to decrease in the density gradient); secondly, the generation of turbulence, due to the vertical shear of the velocity, counteracts the reduction in turbulence, due to the action of the buoyancy force.

For a thinner pool case (the initial pool depth is of 0.01 m), the evaporated mass is much less than compared to a thicker pool case (the
Fig. 11. The variations of the averaged evaporated mass from the pool per unit area $m_{vap}$ (kg/m$^2$) and liquid temperature $T_{liq}$ (K) with time $t$ (s) at a wind velocity of 1 m/s and at initial pool depths $\delta$ of 0.01 m and 0.05 m depending on the pool size $L$: a – benzene; b – toluene; c – ethylbenzene; d – cumene.
Fig. 12. The variations of the averaged evaporated mass from the pool per unit area $m_{\text{vap}}$ (kg/m$^2$) and liquid temperature $T_{\text{liq}}$ (K) with time $t$ (s) at a wind velocity of 2.5 m/s and at initial pool depths $\delta$ of 0.01 m and 0.05 m depending on the pool size $L$: a – benzene; b – toluene; c – ethylbenzene; d – cumene.
initial pool depth is 0.05 m), due to a sharper decrease of the liquid temperature and, as consequence, of the saturated vapour pressure. Depending on the substance and pool size, the estimated evaporated mass at time of 3600 s for the thicker pool is larger by a factor of 1.4-5.2 than the same estimate for the thinner pool at a wind speed of 1 m/s and by a factor of 1.6-4.2 at a wind speed of 2.5 m/s. The higher the boiling point of the liquid is, the greater the effect of the pool thickness on the evaporated mass is. The growth of the evaporated mass decelerates over time, as the cooling of the liquid causes the decrease in saturated vapour pressure and, as a result, in the driving force of mass transfer from the pool surface. The sharper decrease in the liquid temperature and, therefore, in the concentration of vapour above the pool surface explains generally the weaker effect of the pool size on the evaporated mass per unit area for thinner pools, in comparison to thicker pools.

Figs. 11 (a - d) and 12 (a - d) show that, initially, the liquid temperature decreases rapidly, due to intense heat exchange with the environment and significant heat loss by reason of evaporation. As time progresses, the temperature drop rates slow down due to a decrease in the driving force of pool-to-air and pool-to-ground heat transfer and the heat loss by evaporation. It is worth noting that the pool size has a little effect on the time evolution of the liquid temperature, even in cases when the evaporation rate and, hence, the heat loss due to evaporation strongly depend on the pool size. This is explained by the stronger influence of heat sink from the pool to ground on the heat balance compared to the heat loss caused by evaporation.

Quantification of the explosion hazard from flammable liquid spills requires estimating the flammable mass. Flammable mass is the mass of fuel in a vapour cloud that is in the flammable range (Woodward, 1998). In the CFD model the flammable mass (denoted as \( Q_e \)) is computed by summing the product of density, cell volume and the vapour mass fraction for the cells where the volume fraction of vapour is within the lower and upper flammability limits (thereinafter LFL and UFL respectively):

\[
Q_e = \sum_{j=1}^{n} Y_{v,j} \cdot \rho_j \cdot V_j, \tag{24}
\]

where \( n \) is the total number of cells with concentration of vapour within LFL and UFL; \( Y_{v,j} \) is the mass fraction of vapour in the cell centroid; \( \rho_j \) is the vapour-air density in the cell centroid, kg/m\(^3\); \( V_j \) is the volume of the cell, m\(^3\).

The UDF was developed to calculate the flammable mass by Eq. (24) and to plot its value in the Fluent console window.

Figs. 13 (a - d) and 14 (a - d) show time variations of the vapour mass in the cloud within the flammable range at reference velocities of 1 m/s and 2.5 m/s respectively. Initially, the flammable mass \( Q_e \) rapidly grows with time up to a maximum value, and then it decreases, since the evaporation rate decreases due to the reduction of the pool temperature. At the smaller initial thickness of pool, the flammable mass takes less time to reach its maximum and then it decreases faster, because the evaporation rate drops sharper with time.

In case of the thinner pool, the maximum flammable mass decreases with the increase of the boiling point of liquid at both wind speeds under consideration. In case of the thicker pool, there is no such unambiguous dependence of the maximum \( Q_e \) on the liquid boiling point, however, overall, the values of flammable mass from pools of high-boiling liquids somewhat higher than those from pools of low-boiling liquids. The latter is more pronounced at lower wind speed and larger pool sizes. The smaller flammable mass from pools of low-boiling liquids compared to those from pools of high-boiling liquids is linked to the larger fraction of vapours with concentration above UFL. The behaviour of the fraction of the total released mass that is within the flammable range will be discussed in more detail later in the present paper.

Depending on the substance and pool size, at the larger pool depth the peak flammable mass by factor of 1.4-9.1 is larger than the one from a thinner pool at a wind speed 1 m/s and by factor of 1.2-4.9 at a wind speed of 2.5 m/s. The higher the boiling point of the liquid is, the greater the difference is. The differences in the peak flammable mass between thinner and thicker pool cases are directly related to the differences in evaporation rates.

At both pool thicknesses, the flammable mass takes longer to reach its maximum, as the pool size increases. The peak flammable mass is proportional to the pool area with the power from 1.0 to 1.3 at a wind speed of 1 m/s and from 1.19 to 1.26 at a wind speed of 2.5 m/s. Generally, the higher the boiling point of the liquid is, the higher the value of exponent is. Thus, the peak flammable mass increases stronger with the pool area in contrast to the total evaporated mass (Figs. 11 (a - d) and 12 (a - d)).

The higher the boiling point of the liquid is, the steeper reduction of the flammable mass after reaching the maximum is, because the vapour pressure decreases sharper with time. Figs. 13 (a - d) and 14 (a - d) show that for thinner pools of high-boiling liquids the flammable mass drops to zero within a relatively short period (less than 5 minutes) at both wind speeds under consideration, whereas for those of low-boiling liquids at a lower wind speed the flammable mass descends very slowly after some time and has the value greater than zero throughout the period under consideration. Thus, in terms of the dilution rate of the flammable cloud, pools of low-boiling liquids are more dangerous than those of high-boiling liquids, while, as mentioned above, in terms of the maximum value of flammable mass, under certain conditions, the opposite is true.

Overall, at both pool thicknesses, the flammable mass takes less time to reach its maximum as the wind speed increases. At higher wind velocity, the flammable mass decreases faster upon reaching its maximum, because the larger wind velocity improves the dilution of vapour cloud with air. At a higher wind speed, the maximum flammable mass is either higher or close to the one reached at a lower wind speed. This result is obtained due to the compensation of decrease in vapour concentration, because of faster cloud dilution by increasing the supply of vapour from the pool when wind velocity increases. The significantly lower value of the maximum \( Q_e \) for thicker benzene pool of maximum size at a wind speed of 2.5 m/s compared to maximum-sized thicker pools of other substances is due to a higher fraction of vapour with a concentration above the UFL. For benzene, the effects of concentration-induced buoyancy remain significant even at a higher wind speed, because the saturated vapour pressure of the liquid decreases slowly and, hence, the relatively high vapour concentration is sustained in the cloud. In this regard, the conditions for the dispersion of benzene vapours are worse than for vapours of other substances under study, which, as will be shown below, leads to a higher fraction of vapours with the concentration above the UFL and, accordingly, to a decrease in the fraction of vapours with the concentration between LFL and UFL.

The important characteristic of flammable clouds is the fraction of the total released mass which is within the flammable range. Let us denote this quantity by \( Z \). Figs. 15 (a - d) and 16 (a - d) illustrate how \( Z \) depends on time and pool size at reference velocities of 1 m/s and 2.5 m/s respectively. The higher the boiling point of the liquid is and the thinner the pool is, the faster \( Z \) decreases over time (for low-boiling liquids at a lower wind speed upon reaching a maximum) due to a sharper drop in the liquid temperature, and, hence, a sharper decrease in the saturation vapour pressure of the liquid and, as a result, the vapour concentration in the vapour cloud. At a higher wind speed, there is a sharper decrease in \( Z \) over time compared to a lower wind speed case, because in the former case there is a greater fraction of vapours that are dispersed to safe concentrations. In general, with an increase in the pool size, a more gradual change in \( Z \) over time is observed due to the greater mass of vapour released, which leads to its slower dilution to safe concentrations.
For low-boiling liquids at a wind speed of 1 m/s, the fraction of released vapour that is in the flammable range initially decreases and then it increases up to a maximum value. This behaviour of $Z$ is explained by the fact that initially the high vapour pressure of the liquid and weak wind produce concentrations of flammable vapour above the UFL, which reduces the fraction of vapour within the flammable range. As time progresses, a decrease in the evaporation rate leads to a decrease in the mass of vapour with a concentration above UFL and, at the same time, to an increase in the mass of vapour with concentration between LFL and UFL, and, hence, in $Z$. With further decrease in the evaporation rate, the fraction of vapours with concentration below the LFL increases, and, hence, $Z$ decreases after it reaches the maximum value. For low-boiling liquids, the larger fraction of vapours with the concentration above the UFL explains the lower $Z$ values for thicker pools compared to thinner pools in the initial period of evaporation. For high-boiling liquids, the opposite situation occurs, when $Z$ in the initial period of evaporation is higher for thicker pools than for thinner pools. This happens due to the fact that for high-boiling liquids, the saturation vapour pressure decreases more sharply over time compared to low-boiling liquids and, hence, the vapour concentration decreases rapidly below the UFL. Thus, the fraction of vapours with the concentration above the UFL determines the value of $Z$ for high-boiling liquids to a lesser extent than for low-boiling liquids. For high-boiling liquids, the fraction of vapours in the flammable region is determined,
in other conditions being equal, by the total released mass, which is the greater, the greater the pool thickness is. The smaller fraction of vapours with concentration above UFL explains why for thicker pools of high-boiling liquids the fraction of vapours in flammable region is larger than for those of low-boiling liquids in the initial period of evaporation.

The plot of Z (Fig. 16 (a - d)) provides an explanation why the maximum flammable mass for the thicker benzene pool of maximum size has significantly lower values (more than 50%) compared to maximum-sized thicker pools of other substances at a wind speed of 2.5 m/s (Fig. 14 (a - d)). The time at which the maximum $Q_e$ is reached (Fig. 14 (a - d)), the fraction of released vapour in the flammable region for benzene pool ($Z = 0.12$) is significantly lower than that for other substances ($Z = 0.21; 0.44; 0.39$ for toluene, ethylbenzene and cumene pools respectively).

Consequence analysis of accidental releases of flammable substances requires the estimation of the distance over which the release can disperse, maintaining the ability to ignite. It is assumed that this distance corresponds to the distance at which a concentration of half value of the LFL (0.5 LFL) is achieved. Table 5 shows the maximum length of the zone up to 0.5 LFL depending on the substance, wind speed, size and thickness of the pool. The origin of the downwind distance to 0.5 LFL is set at the downwind edge of the pool. For all considered substances, at specified pool thicknesses and wind speeds, the flammable distance in-
The variation of the fraction $Z$ of released vapour in the flammable region with time $t$ (s) at wind velocity of 1 m/s and at initial pool depths of 0.01 m (left) and of 0.05 m (right) depending on the pool size $L$: a – benzene; b – toluene; c – ethylbenzene; d – cumene.

creases with an increase in the pool size. The larger pool thickness yields the larger distance to 0.5 LFL due to the higher evaporation rate. The higher difference in distances up to 0.5 LFL between thinner and thicker pool cases is observed for high-boiling liquids compared to low-boiling liquids: for low-boiling liquids the distance to 0.5 LFL at a pool depth of 0.05 m is 1.15 to 1.49 (1.1 to 2.0) times larger than that at a pool depth of 0.01 m at a lower (higher) wind velocity, whereas for high-boiling liquids it is 2.7 to 4.0 (2.0 to 2.6) times larger than that at a pool depth of 0.01 m at a lower (higher) wind velocity. Overall, for thinner pools, the lower the boiling point of the substance is, the greater the maximum distance up to 0.5 LFL is; however, for thicker pools, under certain conditions, the opposite is true. The smaller flammable distances for thinner pools of high-boiling liquids compared to pools of low-boiling liquids are linked to the fact that the vapour pressure of high-boiling liquids, and, hence, the vapour concentration in the cloud decrease so rapidly that the vapour with flammable concentration does not have time to spread to far distances. A significantly greater flammable distance for pools of high-boiling liquids (ethylbenzene) compared to thicker pools of low-boiling liquids at a wind speed of 1 m/s is explained by the fact that the strong negative buoyancy of clouds in the latter cases hinders the transport of vapour in the downwind direction. Also, thanks to the higher density of the vapour-air cloud, and, as a result, to a more difficult streamwise advection, the flammable distance for the thicker benzene pool of maximum size at a wind speed of 2.5 m/s is significantly lower.
than the flammable distance for thicker pools of toluene and ethylbenzene of the same size.

With exception of thinner pools of cumene, there is no significant difference between predicted maximum downwind distances to 0.5 LFL at wind speeds of 1 and 2.5 m/s: the difference in hazardous distances between higher and lower wind speed cases does not exceed 36%. As for thinner cumene pools, in this case, a wind speed increase leads to a relatively significant increase in the downwind flammable distance (by 40÷89% depending on the pool size), due to the fact that in a very short period of time, during which the maximum flammable mass is reached, higher wind speed provides vapour transport over longer distances compared to a lower wind speed case. The flammable distance is determined by the complex combination of factors, including the vapour pressure decrease and vapour-air cloud buoyancy, therefore, depending on the substance and the pool thickness, a wind speed increase may lead to both a decrease and an increase in the distance up to 0.5 LFL.

It is worth noting that for low-boiling liquids at a wind speed of 1 m/s, the dependencies of the maximum distance up to 0.5 LFL on the pool size are close at a small pool thickness and almost completely coincide at a large pool thickness. Such result can be explained by the fact that the clouds in these cases behave in a similar way due to their strong negative buoyancy.
Table 5. Maximum downwind distance to 0.5 LFL

| Pool size, m | Maximum downwind distance to 0.5 LFL for substance, m |
|-------------|-------------------------------------------------------|
|             | benzene      | toluene     | ethylbenzene | cumene    |
| δ₀ = 0.01 m, U₀ = 1 m/s | 37          | 44          | 23           | 17        |
| 20          | 58          | 55          | 34           | 22        |
| 30          | 67          | 72          | 41           | 24        |
| 40          | 105         | 106         | 72           | 29        |
| δ₀ = 0.05 m, U₀ = 1 m/s | 50          | 51          | 82           | 46        |
| 20          | 73          | 72          | 130          | 64        |
| 30          | 100         | 99          | 162          | 81        |
| 40          | 157         | 157         | 200          | 114       |
| δ₀ = 0.01 m, U₀ = 2.5 m/s | 45          | 33          | 30           | 24        |
| 20          | 66          | 50          | 36           | 34        |
| 30          | 86          | 65          | 52           | 41        |
| 40          | 127         | 94          | 70           | 54        |
| δ₀ = 0.05 m, U₀ = 2.5 m/s | 68          | 66          | 60           | 59        |
| 20          | 94          | 97          | 92           | 84        |
| 30          | 116         | 132         | 122          | 109       |
| 40          | 141         | 193         | 179          | 144       |

4. Conclusions

The CFD model was built and applied to examine the vapour cloud formation from pools of heated organic liquids (benzene, toluene, ethylbenzene and isopropylbenzene) in terms of the evaporated mass per unit area of the pool, the flammable mass of vapours, the fraction of the total released mass that was within the flammable range and the maximum downwind extent of the flammable cloud. The model was validated against published experimental data, and an acceptable agreement was shown. The comparison between evaporation rates from models with different formulations for correction for Stefan flow was performed. It was found that, overall, the model with the mole-based formulation produces a better agreement with experiments compared to the model with mass-based formulation, although, for some experiments, the former tends to underestimate the evaporation rate, while the latter tends to overestimate it.

The results of numerical simulation presented in this work provide a better understanding of evaporation and dispersion processes accompanying the formation of vapour-air cloud due to the evaporation from pools of heated hydrocarbon liquids. The main findings of the numerical study can be summarized as follows:

- The pool size has a considerable influence on the evaporated mass per unit area, especially for low-boiling liquids (benzene, toluene) at a lower wind speed;
- A decrease in the effect of the pool size on the evaporated mass per unit area with a wind speed increase and an initial pool depth decrease is related to the reduction of the buoyancy of the vapour-air mixture;
- For high-boiling liquids (ethylbenzene, cumene), the effect of the pool size on the evaporation is less pronounced compared to low-boiling liquids, because their vapours become more passive with time due to a sharper decrease in the liquid temperature, and, hence, the vapour concentration above the pool surface;
- For a thinner pool case (the initial pool depth is 0.01 m), the evaporated mass is much less compared to a thicker pool case (the initial pool depth is 0.05 m) due to a sharper decrease of the liquid temperature and, as consequence, of saturated vapour pressure. The higher the boiling point of the liquid is, the greater the effect of the pool thickness on the evaporated mass is;
- For scenarios under study, the mass of vapour between flammability limits initially increases up to a maximum value, and then it decreases, since the evaporation rate decreases due to the reduction of the pool temperature. The higher the boiling point of the liquid is and the smaller the thickness of the pool is, the less time is needed for the flammable mass to reach its maximum; and then it decreases faster, because the evaporation rate drops sharper with time;
- In terms of the duration of persistence of a flammable cloud, pools of low-boiling liquids are more dangerous than those of high-boiling liquids, while in terms of the maximum value of the flammable mass, under certain conditions, the opposite is true;
- For heated liquids, the fraction of the total released mass that is within the flammable range during the initial period of evaporation is largely determined by the fraction of vapours with a concentration above the UFL due to high vapour pressure of liquids;
- The larger the liquid boiling point is, the smaller the maximum flammable downwind distance for thinner pool cases is. For thicker pool cases, at certain conditions, the opposite trend is observed because the strong negative buoyancy of vapour clouds from pools of low-boiling liquids hinders the transport of vapour in the downwind direction.

Further research is required to fully understand the mechanisms of vapour cloud formation from pools of flammable and toxic liquids. The proposed pool evaporation model needs to be improved in terms of the limited mixing in the liquid phase. The present model assumes the ideal mixing across a liquid layer height, which may limit its application to evaporation from thick pools of high-viscous liquids such as oil and oil products. Furthermore, the effect of thermal atmospheric stratification on the pool evaporation needs to be investigated in the future study.

CRediT authorship contribution statement

Author contribution statement

Aynur Galeev: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Sergey Ponikarov: Analyzed and interpreted the data; Wrote the paper.

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