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EVAPORATION OF VOLATILE LIQUID POOLS UNDER FORCED CONVECTION:
EXPERIMENTAL APPROACH FOR MULTI-COMPONENT LIQUIDS
AND VALIDATION OF A VAPORIZATION MODEL

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ABSTRACT

The evaporation of pools of volatile liquids under dynamic conditions is gaining interest as an engineering subject. Indeed there is an increasing need to optimize the control of thermal or chemical processes and to cope with more and more stringent Environmental, Health and Safety (EHS) regulations applicable to the handling of hazardous liquids, especially those relating to stationary gas turbine installations. A specific issue, tied with flammable substances, comes from the fact that the transition from a flame to an explosion is not sufficiently well controlled due to the difficulty in modeling complex installations. Therefore, the current approach used to address explosion risks consists in quantifying the flux of vapors emitted by the pool and evaluating the mechanical effect entailed by a potential ignition of the flammable cloud generated. It is therefore of paramount importance to accurately know, under variable vaporizing conditions, how much of the volatile matter is extracted by the ventilation stream from the liquid pool and how these vapors get diluted downstream of the source.

A survey of the literature shows that while pool evaporation of water has been extensively covered by experimentation, most organic liquids including hydrocarbons, alcohols, ethers, etc. have been insufficiently studied. In order to fill this gap, the authors have combined an experimental approach enabling to quantify the source of vapors with a dedicated Computational Fluid Dynamics (CFD) approach describing the mixing/dilution phenomena in the gas phase. This dual approach has proved very fruitful as it leads to realistic spatial distributions of the species downstream of the source. Therefore it has been utilized to develop experimentally

verified data for the evaporation rate of single and multicomponent liquids.

This paper presents the original experimental rig developed to quantify the vaporization rates. The elaboration of the CFD model and the results obtained when coupling both approaches will be the matter of a next paper.

INTRODUCTION

The evaporation kinetics of pools of liquids is gaining interest in process engineering and for EHS purposes as increasingly stringent regulations addressing fire and explosion are being implemented worldwide. Gas turbines are particularly concerned in consideration of the large volumes of liquid fuels handled and the complexity of pipings that make leakage events possible. In such EHS applications, the use of experimentally verified data bases is mandatory. A case of particular relevance is the evaporation in ventilated zones i.e. with a marked contribution of forced convection.

A review of the existing literature shows that while the evaporation of water pools has been the subject of numerous experimental studies, organic substances, even those of daily use such as hydrocarbons, alcohols, ethers, halogenated compounds are very poorly covered. One of the reasons is precisely the potential EHS risks inherent to such evaporation experiments. In addition, there is virtually no literature about the evaporation of multi-component liquids; now most usual liquids such as fuels, solvents, perfumes etc. contain a great number of molecules. Finally, it is often interesting to know the composition of the vapor clouds i.e. the distribution of the concentrations of the individual molecules in it; this is particularly the case in explosion studies where the flammability limits of the cloud depends on its composition.

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For all these reasons, the authors have developed a rational approach to the evaporation of liquid pools. To that end, one has combined an experimental rig designed to quantify the vaporization of multi-component liquids under forced convection with a suitable CFD model accounting for the transport phenomena in the gas phase. This approach appeared to be very fruitful. Indeed it has provided on one hand a valuable tool to obtain experimental vaporization kinetics data for a wide range of liquids and on another hand, an interesting description of the vapor clouds, including the iso-concentration surfaces of the individual molecules downstream of the source. This paper sets out the development of the experimental rig used for the experimental vaporization studies. The CFD model used to deal with the mixing processes in the gas phase and the coupling of both approaches will be covered in a next paper.

VAPORIZATION MODELS

1- The basic physics of evaporation:

Real evaporation processes are generally a combination of “free convection” and “forced convection”. Free convection is the sole practical transport process in a quiet atmosphere while forced convection is caused by wind or a ventilation stream. In a forced convection regime, the motion of the surrounding air accelerates the transfer of the volatile species from the liquid (“L”) into the gas phase (“G”) by permanently depleting the boundary layer that stays saturated in volatile species. Free convection intervenes only if the density of the vaporized species is lower than that of the air stream which is the condition to create the buoyant Archimedes forces; this is the case for water but rarely for most organic compounds that are heavier than air. The physics of evaporation involves the sequence of two distinct steps that are:

- (i) the thermal transfer of the volatile species from the liquid to the air through the L/G interface which represents the “source term” and will be designated in this paper by the term of “vaporization”; this aspect is the main subject of the present paper

- (ii) the diffusive/turbulent motion of these vaporized species by and within the gas stream (the “transport term”).

For the sake of clarity, the combination of the two steps will be referred to as the “evaporation” process.

This paper deals with vaporization of pools in air streams and is restricted to stationary conditions. We will not cover boiling pools which means that the temperature of the air stream will be lower than the initial boiling point of the liquid; it will also be assumed that evaporation does affect the pool temperature, corresponding to moderate evaporation kinetics.

Most models developed up to now for evaporation processes, starting from the early work by Carrier [1] characterize the rate of transfer “ J_i ” of the volatile molecule “ M_i ” from the liquid to the air in using two terms:

- a “driving potential” term that expresses the difference ($C_i^{sat} - C_i^\infty$) where “ C_i^{sat} ” is the saturated concentration that would be developed by the volatile species “ i ” in the atmosphere at the equilibrium and C_i^∞ is its actual concentration in the incoming air. The term C_i^{sat} represents the “vaporization potential” of the pool and is defined at the temperature T_L of the liquid bulk and not at the temperature of the L/G interface.

- a “transfer coefficient” h_i that characterizes the exchange rate of the molecules M_i between the liquid and the gas and depends on local aerothermal conditions. One often uses mass transfer coefficients but in the calculation of flammability limits, the use of molar transfer coefficients “ $h_{i,mol}$ ” is more practical. Therefore, the flux of volatile matter through the interface writes:

$$J_{i,mol} = h_{i,mol} * (C_i^{sat} - C_i^\infty) \quad (1)$$

$J_{i,mol}$ is in [$\text{mol s}^{-1} \text{m}^{-2}$]; C_i^{sat} and C_i^∞ in [mol/m^3]. Therefore, $h_{i,mol}$ has the dimension of [m s^{-1}].

2- Pauken’s vaporization model:

The “vaporization problem” equals to evaluate the molar transfer coefficient “ $h_{i,mol}$ ” in the case of stationary pools (the vaporization of drop clouds is not the subject of this paper) Numerous works exist, essentially for the vaporization of water [1-18]. The present work will rely on an up-to-date, experimental and theoretical work published by Michael Pauken [2].

The following notation will be used: “L” denotes the liquid and T_L its temperature. “L” contains “n” species M_i the molar fractions of which are $\{x_i\}$ in the liquid phase and $\{y_i\}$ in the vapor cloud. The concentration of M_i in the incoming air “ C_i^∞ ” is generally zero. Finally “U” is the speed of the air stream and T^∞ , ρ^∞ and μ^∞ its temperature, density and dynamic viscosity far upstream from the pool.

It is also necessary to define some properties of the thermal boundary layer: T_{bl} is the temperature; one usually takes $T_{bl} = (T^\infty + T_L)/2$; ρ_{bl} and μ_{bl} are respectively the local density and dynamic viscosity of the air (free of vapor) while ρ_{sat} is the density of the air saturated with vapor at the same temperature T_{bl} .

The flux of volatile matter through the L/G interface is given by equation 1 above, in which the coefficient $h_{i,mol}$ writes:

$$h_{i,mol} = Sh_i D_{ia}/L \quad (2)$$

where:

- (i) the Sherwood number “ Sh_i ”

- (ii) the diffusivity of the molecule M_i in the air “ D_{ia} ” (defined at the “bl” conditions)

- (iii) a characteristic length of the pool (“L”)

The diffusion coefficient “ D_{ia} ” of the species M_i in air can be calculated using an equation recommended by Prausnitz [19].

The Sherwood number “ Sh_i ” depends from a number of properties of the system including the type of convection. In the case of a pool with infinite width, Sh_i writes:

- for free convection:

$$Sh_{i,free} = k_a (Sc \cdot Gr)^a \quad (3a)$$

where the numeric constants k_a and a depend from the convection regime (laminar or turbulent)

- for turbulent forced convection:

$$Sh_{i,forced} = k_b \cdot Sc^{1/3} \cdot Re_L^b \quad (3b)$$

where $k_b = 0.036$ and $b = 0.8$.

Sc, Gr and Re_L are respectively the Schmidt, Grashof and local Reynolds numbers; their definitions are as follows:

$$Sc = \rho_{bl} / (\mu_{bl} \cdot D_{ia}) \quad (4)$$

Sc characterizes the relative effects of gravity and diffusion.

$$Re_L = \rho^\infty \cdot U \cdot L / \mu^\infty \quad (5)$$

Re_L characterizes the flow regime close to the pool, U being the air velocity and L a characteristic dimension of the pool.

$$Gr = \rho_{bl} \cdot (\rho^\infty - \rho^{sat}) g L^3 / \mu_{bl}^2 \quad (6)$$

Gr characterizes the driving force for free convection that exists only if the density of the saturated air exceeds that of the pure air: $(\rho^\infty - \rho^{sat}) > 0$

In the case of finite pools with specific geometry, Sh_i must be factored by a geometric coefficient.

In the (frequent) case of mixed free and forced convection, the net Sherwood number can be expressed as a combination of both categories:

$$Sh_i = [(Sh_{i,free})^n + (Sh_{i,forced})^n]^{1/n} \quad (7)$$

where $n = 2$ according to Pauken [2].

In the case of turbulent forced convection and when free convection is inexistent i.e. when the M_i is heavier than air (which is the case for organic substances), one has simply, for a circular pool:

$$Sh_i = Sh_{i,forced} = 0.040 Sc^{1/3} Re_L^{0.8} \quad (8)$$

where Sc and Re_L are given by equations 4 and 5.

EXPERIMENTAL RIG

1- Design criteria:

The scarce data available for the vaporization of organic substances, including hydrocarbons, has led the authors to design and build a dedicated “vaporization rig” able to cover a large variety of molecules as well as mixtures: hydrocarbons (e.g. gasoline or naphtha with variable composition; kerosene and diesel oil); alcohols (e.g. ethanol, methanol and butanol); ethers (e.g. DME); esters (e.g. SME); halogenated compounds etc.

The key design criterion of the rig developed has been to create an L/G interface of well defined geometry and at which the aero-thermal conditions of the air and the liquid are strictly controlled. These conditions are: (i) the speed, temperature and flow regime of the air (ii) the temperature and composition of the liquid.

Some additional design criteria were applied:

- minimize the foot print of the rig to reduce cost and facilitate installation and operation
- minimize the volume of the model pool to suppress EHS issues during the experiment

- use glass as construction material to enable a full visualization of the experiments

- achieve the shortest experiment duration

This rationale has resulted in the rig sketched in **figure 1** that shows a simple, essentially linear, cylindrical train of internal diameter 20 cm.

2- Description:

The evaporation rig consists of 8 sub-systems achieving each a specific function (**figure 1**):

- 1- a heating/ventilation system (a fan equipped with an internal heater)
- 2- a vortex breaking section intended to annihilate the eddies generated by the fan
- 3- a diffuser providing a progressive increase of duct section
- 4- a “tranquilization” zone made by an array of thin, parallel tubes that tend to impart a mono-dimensional, uniform speed vector
- 5- a working zone in which vaporization occurs
- 6- a homogenization zone in which the vapors and the air are thoroughly mixed
- 7- a sampling zone (7) coupled with an analysis train (7.1)
- 8- an evacuation zone

The master piece of the rig is the working zone (item 5 in figure 1) a photograph of which is shown in **figure 2** and which consists of a “vaporization chamber” (5.1) and an “auxiliary chamber” (5.2). These chambers are separated by a horizontal plate (5.3) and are swept along by the air stream that features an essentially axial, uniform speed vector (generated by the tranquilization zone) and a uniform temperature. The respective flow rates in the vaporization and auxiliary chambers are determined from speed measurements using hot wire sensors. A circular window (5.4) has been bored in the horizontal plate in order to allow the emergence into the vaporization chamber of the top of a cylindrical “circulation vaporization cell” (5.5) or CVC. This CVC is filled with the liquid and creates a circular pool of small diameter (2cm). In order to keep its level constant, the liquid of the pool is equipped with an overflow device and is continuously circulated by a pump (5.6) within an external circuit that features a graduated reservoir (5.7). With this design, the free surface of the liquid pool is kept at the same level (“z”) as the upper wall of the separation plate so that it is continuously swept by the tangential ventilation stream, under controlled temperature and speed conditions. The temperature of the liquid having the selected composition is also monitored by a thermocouple and can be independently controlled by means of a small heater (or a cooler) (5.8). The quantity of liquid vaporized is directly measured by the drop of the liquid level in the graduated reservoir (5.7).

In addition to this very simple determination of the vaporization rate, another essential capability of this rig is the possibility to speciate the molecules contained in the vapors. Indeed, while the field of the concentrations of the molecule M_i just downstream of the cell (5.5) is highly stratified (vapor concentrations decrease with increasing z), the mixing zone (6) renders this field fully uniform so that any gas sample extracted in zone (7) through the sampling line (7.1) is representative of the average concentration of the vapors in the stream.

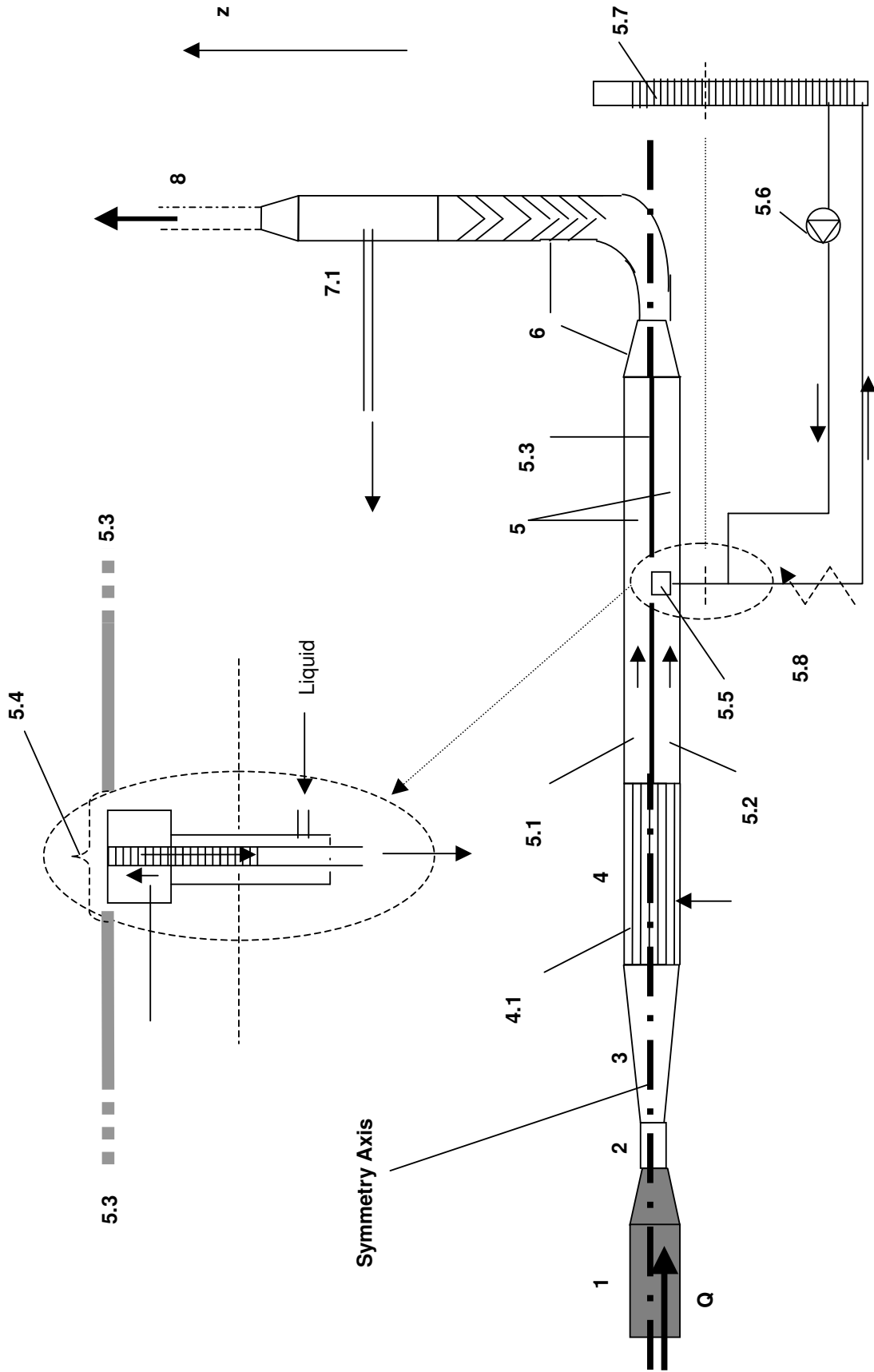


FIGURE 1: Sketch of the vaporization rig

amounts $6.52 \pm 0.03 \text{ ml/h/cm}^2$ equaling $(4.30 \pm 0.02) \text{ g/h/cm}^2$ (density of n-hexane: $0,6594 \text{ g/cm}^3$)

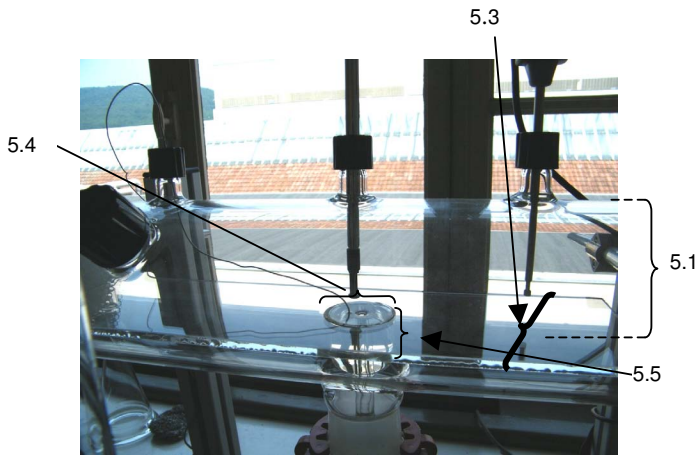


FIGURE 2: View of the working zone of the vaporization rig

Therefore the total vapor concentrations can be continuously measured using e.g. an FID (flame ionization detector) connected to line 7.1; in addition, each individual concentration of the molecule M_i can be measured either in a continuous way by mass spectrometry or in a discontinuous way by condensing the vapors in a cryogenic trap and subsequently analyzing the trapped mixture.

EXAMPLES OF USE OF THE RIG

Figure 3 and 4 illustrate an example of experimental data obtained with the rig.

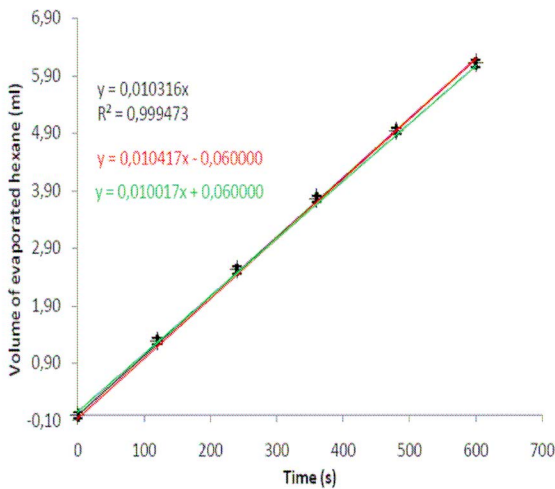


FIGURE 3: n-hexane vaporized volume versus time

The particular case shown refers to the vaporization of n-hexane in the following conditions:

$$U = 0,92 \text{ m/s}; T^\infty = 45^\circ\text{C} \text{ and } T_L = 23,5^\circ\text{C}.$$

Figure 3 shows the volume of liquid evaporated versus time whereas figure 4 illustrates the monitoring of the air temperature and speed during the experiment. One can verify that, for such a mono-component liquid vaporizing in stationary conditions, the rate of vaporization remains constant. At the temperature and speed of the experiment, this vaporization rate

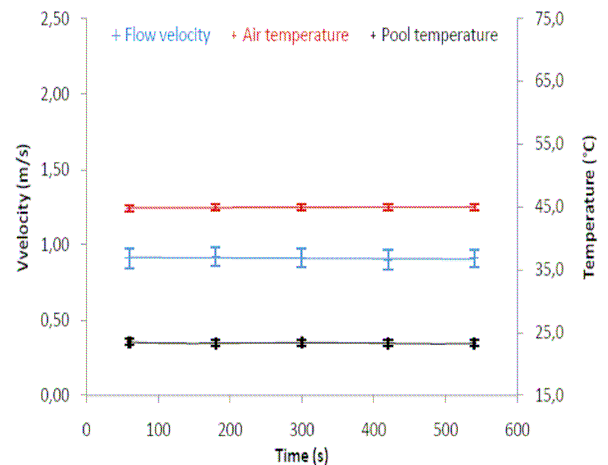


FIGURE 4: test parameters monitoring during n-hexane vaporization

More generally, the rig has allowed obtaining, after a short experimental work, the experimental vaporization data for ethanol and 5 hydrocarbons having increasing boiling points (C_6-C_{12}).

Figure 5 shows the vaporization rates obtained when using respectively the experimental rig (J_{exp}) and Pauken's calculation model (J_{th}).

The correlation obtained:

$$J_{exp} = 0,977 \cdot J_{th} - 0,02 \quad (9)$$

It is valid over the 2.7 decades and features a correlation coefficient of 0.99.

This shows that both data series are very close.

The concrete result of this short study is that Pauken's model tends to very slightly over-predict the real vaporization rate ξ . Therefore, it is possible for safety studies, to rely on this slightly conservative model for the description of the vaporization step.

PROSPECTS:

The overall "evaporation problem" in stationary conditions is fully solved only when one has access to the field of concentration $\{Y_i\}$ for each individual volatile species in the space surrounding the pool. In particular, the isopleths (or iso-concentration surfaces) of each species give a valuable representation of the vaporization clouds and since we are in stationary conditions, these isopleths are invariable over time. When studying inflammation/explosion scenarios, the Lower Flammability Limit (LFL) is the most relevant data so that the "iso-LFL" surfaces can replace the isopleths. The LFL of a mixture of gases or vapors can be expressed in function of the LFL's of the individual species and their mole fractions (y_i) by a formula known as the "Le Châtelier law":

$$1 / LFL = \sum(y_i / LFL_i) \quad (10)$$

Therefore the knowledge of the spatial distribution of the y_i 's enables determining the iso-LFL surfaces. The problem of determining the spatial distribution of the vapor molecules equals to solve the equations that rule their migration in the air phase by diffusion and turbulence, i.e. their transport

by the air stream and their mixing inside this stream. This task has been achieved using two distinct CFD codes: Comsol® and Fluent®. The result of this second activity and the coupling of both approaches will be the subject of a next paper.

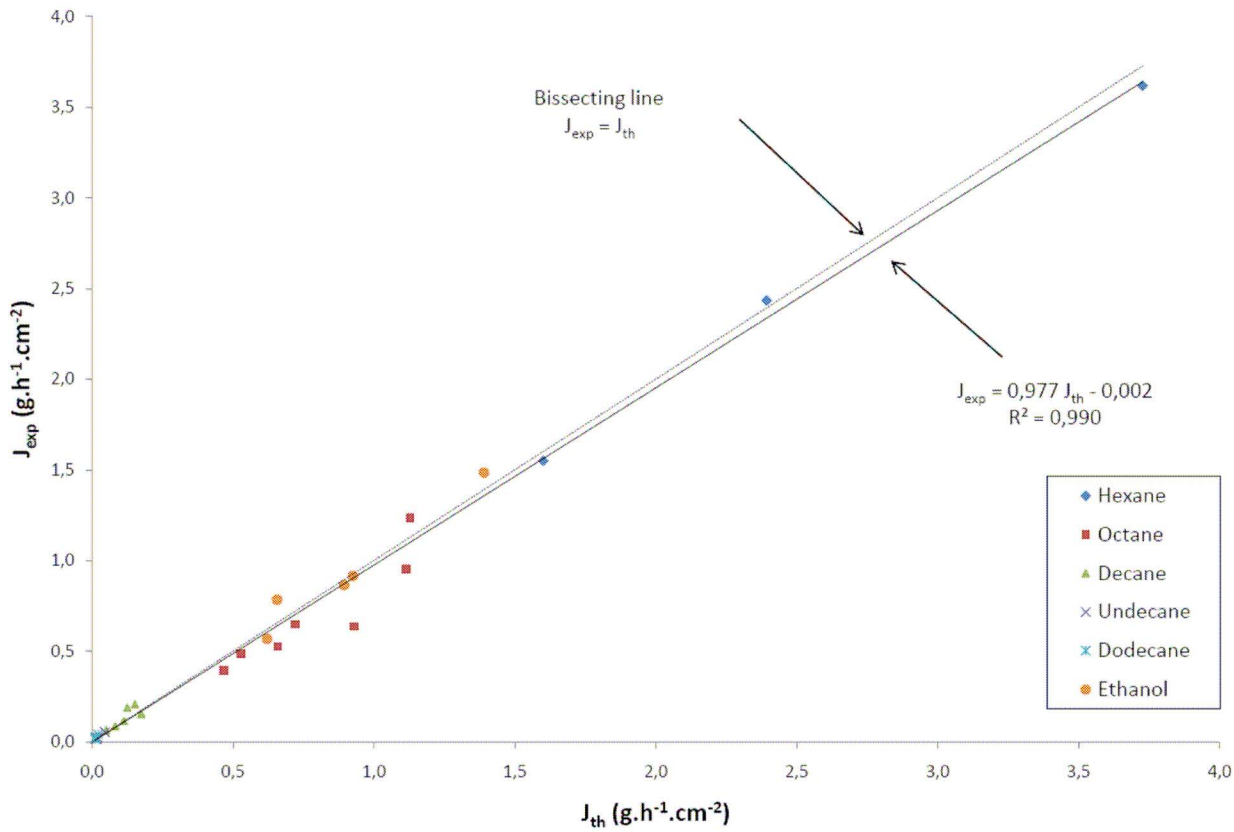


FIGURE 5: Correlation between the vaporization rates of some liquids obtained experimentally with the vaporization rig (ξ_{exp}) and (ii) after Pauken (ξ_{th})

CONCLUSION

This paper has covered the task of getting experimental transfer coefficient data relating to the vaporization of liquid pools containing a large variety of volatile molecules and exposed to variable aero-thermal conditions. The creation of an original, flexible, small-size vaporization rig has allowed to validate, in safe conditions, an up-to-date model that was originally devised for water.

This work is the first part of a more global program in which this local vaporization model is coupled with a dedicated CFD approach intended to predict the characteristics of the vapor clouds around the liquid pool. This second task along with some illustrative examples will be reported in a next paper. The overall work is of special interest for stationary gas turbine installations in which a liquid fuel is often used, the storage, pumping and transfer of which generates risks of leakages that are part of specific safety analyses.

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NOMENCLATURE

- a : Sherwood number model parameter [-]
b : Sherwood number model parameter [-]
C : concentration [mol.m⁻³]
D : diffusivity [m.s⁻²]
h : molar mass transfer rate [m.s⁻¹]
k_a, k_b : Sherwood number model parameter [-]
Gr : Grashof number [-]
L : characteristic length [-]
n : Sherwood number model exponent [-]
Re : Reynolds number [-]
Sc : Schmidt number [-]
Sh : Sherwood numbers [-]
T : temperature [°C]
U : air stream velocity [m.s⁻¹]
y : mole fractions [-]

Greek Letters

- μ : dynamic viscosity [Pa.s]
ρ : density [kg.m⁻³]

Subscripts

- a : air
bl : boundary layer
free : free convection
forced : forced convection
G : gas phase
i : ith component of the hydrocarbon mixture
L : liquid phase

Superscripts

- sat : saturated air
∞ : incoming air

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