

On the Time to Flaming of Flammable Liquids

Benedetta Anna De Liso, Gianmaria Pio, Ernesto Salzano*

Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, Via Umberto Terracini 28, 40131 Bologna (Italy)

ernesto.salzano@unibo.it

Flammable liquids typically adopted in chemical and industrial processes can be subjected to intense heat radiation due to nearby hot surfaces or fires. A second cascading event is then likely because the flash point can be easily reached and the surrounding environment can provide sufficient energy for ignition. Nevertheless, the flaming condition is not necessarily reached instantaneously if no direct (e.g., spark) ignition is present. Hence, a time to flaming, i.e., in the absence of an ignition source, is extremely relevant for the active and passive fire protection of flammable liquid, as the minimum time for intervention can be defined before developing a pool fire and for the correct evaluation of domino effects, in analogy with gas fires. In addition, a complete characterization of liquid behaviour under radiant heating is essential to guarantee safe operations, prevention measures, robust databases and optimized design. Therefore, this work reports the results for three liquid solvent representative classes of substances: i) hexane, ii) ethyl acetate, and iii) ethanol. A bench scale facility was adopted for the characterization of mass and energy aspects involving a pool fire of the investigated substances. Among the others, the ignitability and the intensity of the generated pool fires were evaluated experimentally in terms of mass burning rate, heat release rate, and combustion efficiency. Different boundary conditions were tested to identify the optimized set of conditions for a robust evaluation of the safety aspects of liquid. Results showed the most relevant trends in terms of ignitability of liquid species and combustion intensity during the pseudo-steady state regime of a pool fire. In addition, indications on the boundary conditions to be considered for a robust and consistent dataset were provided in this work.

1. Introduction

Within the intricate landscape of the chemical industry, the strategic utilization of liquid solvents is integral to a multitude of processes, spanning from chemical synthesis to separation reactions and beyond. In addition, the renewed interest in energy storage systems for a more sustainable supply chain involving liquid solvents has introduced alternative formulations and operative conditions within the available applications for flammable liquids. Hence, a nuanced exploration of the inherent risks associated with these solvents at each stage of their lifecycle is indispensable for ensuring operational efficiency and safety (Rogers, 1996).

Handling and transportation of these solvents unveils a potential minefield of hazards, ranging from leakage and dispersion to the formation of flammable atmospheres. Based on the presence of an immediate or delayed ignition source or its absence, different scenarios can be considered, as described in detail in well-established literature (Uijt de Haag, P. A. M., & Ale, 2005). The dynamic interplay of several factors including volatility, vapour pressure, and reactivity during transit necessitates a meticulous risk assessment and consequence analysis (Stojadinović et al., 2023). In this sense, understanding the physicochemical properties of solvents is essential for implementing effective preventative measures against potential spills or accidents (Liaw et al., 2010).

The spectre of accidental scenarios, notably pool fires, looms large during the handling and storage of these solvents. The formation of a combustible liquid layer on a flat surface poses a substantial risk, with the potential for catastrophic consequences (Vali et al., 2014). The repercussions are two-fold: the flash point is easily attained, and the ambient environment provides sufficient energy for potential ignition, initiating a sequence of events that may lead to severe consequences (Jenft et al., 2014). The time it takes for a flammable liquid to transition into a flaming state, especially in the absence of a direct ignition source, emerges as a paramount

consideration. This temporal aspect, known as the time to flaming, plays a pivotal role in shaping effective strategies for both active and passive fire protection measures together with the overall reactivity (De Liso et al., 2023). Unlike scenarios involving immediate ignition sources like sparks, the path to a flaming condition is nuanced and necessitates a specific analysis of the temporal dynamics involved. Indeed, the evaluation of the possible auto-ignition as well as ignition delay can represent a paramount step, in agreement with the classical approach implemented for solid- (Van Wingerden, 2019), gaseous- (Pio et al., 2022), and dust-related fires (Hagen and Meyer, 2021).

A pool fire is characterized by the establishment of a diffusion flame on top of a horizontal fuel where buoyancy forces, turbulence and molecular diffusion are all transport mechanisms. Mass burning rate, flame radiation properties, such as emissivity and temperature, and flame geometrical characteristics including height, shape and diameter, are dominant factors in the determination of thermal radiation flux from pool fires (Joulain, 1998). Besides, robust databases for these parameters can have beneficial effects on the accuracy of advanced numerical simulations (Pio et al., 2019). In this context, experimental assessments become indispensable, shedding light on the intricacies of flammable liquid behaviour under radiant heating (Chen et al., 2021). The significance of such evaluations is underscored by their ability to define a minimum intervention time, providing a critical window before the escalation to a pool fire. This temporal insight is crucial not only for mitigating immediate risks but also for evaluating domino effects, aligning with established practices in gas and dust fire assessments (Florit et al., 2022).

Extensive research has demonstrated that the pool diameter plays an essential role in the dynamics and consequences of a pool fire (Chen et al., 2023). Indeed, different governing burning modes can be attributed based on the analysed range. More specifically, Babrauskas (1983) (Babrauskas, 1983) attributed convective laminar flames to pools having a diameter smaller than 5 cm, convective turbulent flame to pools having a diameter within the range of 5 – 20 cm, radiative optically thin flames to pools having a diameter included in 20 – 100 cm, and radiative optically thick flames for pool larger than 1 m as a diameter. Quite obviously, the validity of these ranges can be affected by the chemical composition of the analysed flammable substances. Regardless of the classification, the population of experimental databases have allowed for the development of empirical correlations for a preliminary assessment of the main combustion characteristics of a pool fire. As a way of example, the pioneering work of Hottel (Hottel, 1959) is worth mentioning. Indeed, the resulting correlations for the evaluation of the mass burning rate and flame height as a function of the pool diameter are still considered a benchmark for further developments (Pio et al., 2019b). However, considering the scope of the posed target, most of the available experimental tests can suffer from uncertainties, unpredictability, or discontinuity of boundary conditions, especially in the case of large-scale tests. In this sense, the realization of a robust database at small or medium scales can be recommended. Besides, the production of a controlled and monitored atmosphere can be highly desirable to generate experimental data suitable for the development of specific models and correlations reproducing industrial-relevant conditions. In this sense, defining the intensity of external heat flux reaching a liquid at a temperature above its flash point is paramount (DiDomizio et al., 2021). Therefore, an in-depth analysis of the thermal and combustion properties of solvents is imperative to develop predictive models that can inform safety protocols.

Zooming in on specific solvents, hexane, ethyl acetate, and ethanol emerge as exemplars, each exhibiting distinct characteristics that influence their response to external stimuli. Hexane, a hydrocarbon solvent, is known for its low flash point (T_f : $-23\text{ }^\circ\text{C}$, (Cameo, 2023)), indicating its susceptibility to ignition at relatively low temperatures. Frequently employed in industrial processes such as extraction and cleaning (Malekshah et al., 2023). Similarly, ethyl acetate, a commonly used solvent with applications in paints, coatings, and adhesives (Tarantola et al., 2023), exhibits specific characteristics, including a moderate flash point (T_f : $-4.4\text{ }^\circ\text{C}$, (Cameo, 2023)). Ethanol (T_f : $12.7\text{ }^\circ\text{C}$, (Cameo, 2023)), a biofuel and industrial solvent, introduces a multifaceted dimension to the discussion. With its application in the automotive sector as a fuel additive, ethanol transportation raises intricate safety considerations (Kolhe et al., 2023). The experimental exploration of these solvents requires sophisticated methodologies, and the cone calorimeter emerges as a cornerstone in unravelling their combustion behaviour. This apparatus facilitates a detailed analysis of heat released, mass loss, and combustion characteristics, providing invaluable insights into how these solvents respond to varying heat intensities (Madani et al., 2023).

For these reasons, this work presents an experimental campaign devoted to the assessment of the main parameters relevant to the characterization of a pool fire at a bench scale. To this scope, an innovative and reproducible procedure was developed to guarantee the uniformity and robustness of the obtained results. This aspect is essential to populate a database suitable for fruitful comparison of flammable liquids as well as for the realization of accurate models dedicated to the consequence analyses.

2. Methodology

To delve into the complexities of heterogeneous phenomena involved within a pool fire, specialized techniques such as the Cone Calorimeter come to the forefront for a bench scale. This instrument, exemplified by the iCone+ developed by Fire Testing Technologies Ltd. (UK), facilitates controlled experiments that enable a detailed analysis of fire behaviour for distinct classes of flammable substances. The abovementioned system and the corresponding protocol (ISO 5660, 2019), including the calculation of uncertainties, have been extensively adopted for the characterization of flame behaviour of solid samples (Quan et al., 2022), with few applications for the liquid case (DiDomizio and Weckman, 2016). However, in this work, an innovative procedure was proposed and implemented to allow for the evaluation employing a cone calorimeter equipment item of liquid solvents, as well. This procedure was implemented for the evaluation of pool fires of hexane, ethyl acetate, and ethanol. All the investigated compounds were purchased by Sigma-Aldrich at the maximum purity degree ($\geq 99\%$).

The samples were exposed to constant heat fluxes ranging from 7 to 50 kW/m² by a cone-shaped resistance and non-immediately ignited by the provided electrical sparkler. The specimen was posed in a standardized sample holder having a squared basis with a surface area of 100 cm² at 2.5 cm from the heat source. A liquid pool having an initial thickness of 1 cm was considered for all tests. The main combustion parameters involving either the mass or the energy aspects were monitored by the experimental system. More specifically, the profiles of mass and mass burning rate with respect to time were measured through a load cell. The exhaust gases were conveyed in a dedicated duct system by a vacuum pump imposing a constant volumetric flow rate of 24 L/min. The resulting gaseous mixtures were analysed by using an IR analyser and paramagnetic analyser to monitor the content of carbon monoxide, carbon dioxide, and oxygen, as well as utilizing a He-Ne laser photometer beam for the assessment of soot formation. The heat release rate was calculated based on the oxygen consumption method derived from direct measurements of the oxygen volumetric fraction and the flow rate of the exhaust gas. To this scope, specific calibrations were carried out to determine the orifice constant coefficient C at operative conditions relevant to the experimental campaign described in this section. Eventually, pressure and temperature profiles within the duct dedicated to the exhaust gases were monitored by conveniently placed thermocouples and barometers.

The acquired data were compared with experimental measurements from the current literature, once available, and empirical correlations. The flame shape and radiative intensity of pool fire are closely related to the burning rate of fuels which is commonly represented by the mass burning rate per unit area. As mentioned before, the combustion rate of usual hydrocarbon fuels can be estimated through well-known correlation (Hottel, 1959) depending on the diameter of the liquid pool (D_p) and other characteristics such as the absorption-extinction coefficient ($k\beta$) of the flame (Eq(1)).

$$MBR = MBR_i(1 - e^{-k\beta \cdot D_p}) \quad (1)$$

Besides, the dimensionless number B accounts for the ratio between the heat of gasification required to reach the boiling temperature starting from the atmospheric conditions (Δh_g) and the measured effective heat of combustion (EHC), i.e., the energy produced by combustion per unit of consumed mass. It was defined for the sake of uniformity in the comparison of different species (Eq(2)).

$$B = \frac{EHC}{\Delta h_g} \quad (2)$$

Alongside the experimental data, an additional parameter was included, labelled as the flux time product. The latter is calculated as the product of the time to ignition, the external heat flux and the exposed sample surface area (Eq(3)), following the definition provided in the current literature (DiDomizio et al., 2021).

$$FTP = t_{ig} \cdot q_e \cdot A_s \quad (3)$$

where t_{ig} , q_e , and A_s are respectively the time to ignition, the external flux provided to the sample, and the sample area exposed to the flux. The latter is assumed as a constant throughout the whole experimental campaign and corresponds to the internal area of the specimen.

3. Results

Regardless of the investigated conditions or components, growth, pseudo-steady state and decay phases can be distinguished within the mass and energy profiles. The intensity, duration and shape of the measured variations are mostly determined by external heat flux and chemical formulation analysed. For the sake of consistency, in the experimental investigation conducted in this work for the characterization of bench scale pool fires of ethanol, hexane, and ethyl acetate, the results obtained under critical flow conditions and in the

quasi-steady state of fully developed combustion are disclosed. More specifically, a critical flow is defined as the minimum external heat flux required to produce a stable and self-sustained flame in the absence of an external ignition source (Tahmid Islam et al., 2023). This definition has been largely considered for biomass characterization, with typical values included within the range of 15 kW/m² and 25 kW/m² (DiDomizio et al., 2021). Nevertheless, to the best of our knowledge, no indications are available on this parameter for the investigated liquids. In addition, Table 1 included the critical heat flux (q_c), the heat release rate (HRR), the mass burning rate (MBR), the effective heat of combustion (EHC), the ratio of the yield of carbon monoxide and carbon dioxide (CO/CO₂) and the specific smoke extinction area (SEA). The latter is based on the measured light extinction coefficient, volumetric flowrate of exhaust gas, and MBR, as described in detail into the dedicated standard (ISO 5660, 2019).

Table 1: Main parameters obtained by cone calorimeter test at critical heat fluxes for each solvent in the quasi-steady-state phase.

	q_c [kW/m ²]	HRR [kW/m ²]	MBR [kg/s]	EHC [MJ/kg]	CO/CO ₂ [kg/kg]	SEA [m ² /kg]	FTP [kJ]
Ethanol	35	805	$0.32 \cdot 10^{-3}$	24.98	0.002	0.67	1.75
Hexane	25	2728	$0.59 \cdot 10^{-3}$	46.40	0.017	8.22	3.75
Ethyl acetate	25	305	$0.17 \cdot 10^{-3}$	17.90	0.016	4.87	43.75

q_c : critical heat flux; HRR: heat release rate; MBR: mass burning rate; EHC: effective heat of combustion; CO/CO₂: carbon monoxide and carbon dioxide ratio; SEA: smoke extinction area; FTP: flux time product.

Ethyl acetate and hexane exhibit a lower critical heat flux (q_c) compared to ethanol, indicating a higher propensity to ignite at lower heat flux levels. This is particularly relevant if compared with the flash point of each component. Indeed, although the flash points of hexane and ethyl acetate are significantly different, no variation in critical flux can be observed for these species. The flux time product (FTP) values offer a distinctive lens into the energetic aspects of ignition and combustion for each solvent, referring to the total energy imparted to the specimen from external heating before ignition. The higher FTP for ethyl acetate implies a more prolonged and energetically demanding ignition, potentially influencing fire dynamics. Considering the lower heat flux provided to the sample, this aspect can be attributed mostly to the thermal inertia of the system. Meanwhile, the lower FTP values for ethanol and hexane suggest relatively shorter ignition processes.

Once dealing with the energy production at a steady state condition, the heat release rate (HRR) for hexane is significantly higher in its critical conditions than the Ethanol and Ethyl acetate, because of a more intense combustion process demonstrated by the trend in the effective heat of combustion (EHC). This aspect has positive feedback on the production of vapour, as demonstrated by the similar trend observed for the mass burning rate (MBR). These aspects indicate a comparatively slower and less energy-efficient combustion possibly influenced by the ester functional group in its structure: the presence of the ester bond and oxygen contributes to a distinctive combustion profile. The carbon monoxide and carbon dioxide ratio (CO/CO₂) is highest for Hexane, in line with its aliphatic structure, emphasizing its proneness for incomplete combustion. The elevated smoke extinction area (SEA) of hexane suggests a greater dispersal of combustion smoke produced per unit mass. The lower SEA values for ethanol and ethyl acetate imply a more contained release of combustion byproducts per unit mass, pointing towards a potentially more controlled and manageable oxidation for these species.

Figure 1 reports the mass burning rate at the steady state obtained in this study and retrieved from the current literature at different pool diameters and solvents as a function of the B-number, previously defined in Eq(2).

At this stage, it is worth mentioning that the data gathered from the literature do not include any indications of the external heat flux provided to the sample, as well as a limited set of information on the atmospheric conditions during the reported tests, with obvious implications on the accuracy of these data. For the sake of completeness, a trend line representative for the MBR for large pools reported in the literature (blue line) and a trend line for MBR data retrieved for a pool diameter of 20 cm (red line) were reported above together with the one corresponding to an equivalent pool diameter of 11 cm (green line), i.e., the one referring to the newly collected data.

Focusing on the reported data for hexane, the collected value is included within the data from the literature although it corresponds to the smallest diameter. Hence, this trend cannot be caught by the correlation proposed by Hottel. However, this discrepancy stems from the analyzed diameter being situated in a region dominated by convective turbulence, where the burning rate typically demonstrates an increasing trend as the pool diameter decreases (Chen and Wei, 2014). This empirical observation extends to ethanol, highlighting that the influence of diameter on the mass burning rate is non-negligible, contrary to assumptions made in previous works (Gosse, 2000).

Noteworthy, a linear trend can be identified for the MBR experimentally collected in this work as a function of the dimensionless number B. This is particularly relevant from the perspective of a possible standardized procedure for the characterization of pool fires. Indeed, the MBR is affected by the external heat flux provided to the sample. However, the values documented in existing literature lack clarity or, at the very least, disregard the thermal flux to which the liquid is exposed, a crucial factor that can be measured and controlled in cone calorimeter tests. Therefore, the use of the critical flux as a boundary condition, as proposed in this work, reduces the degree of freedom during the experimental campaign and allows for rigorous and robust analysis.

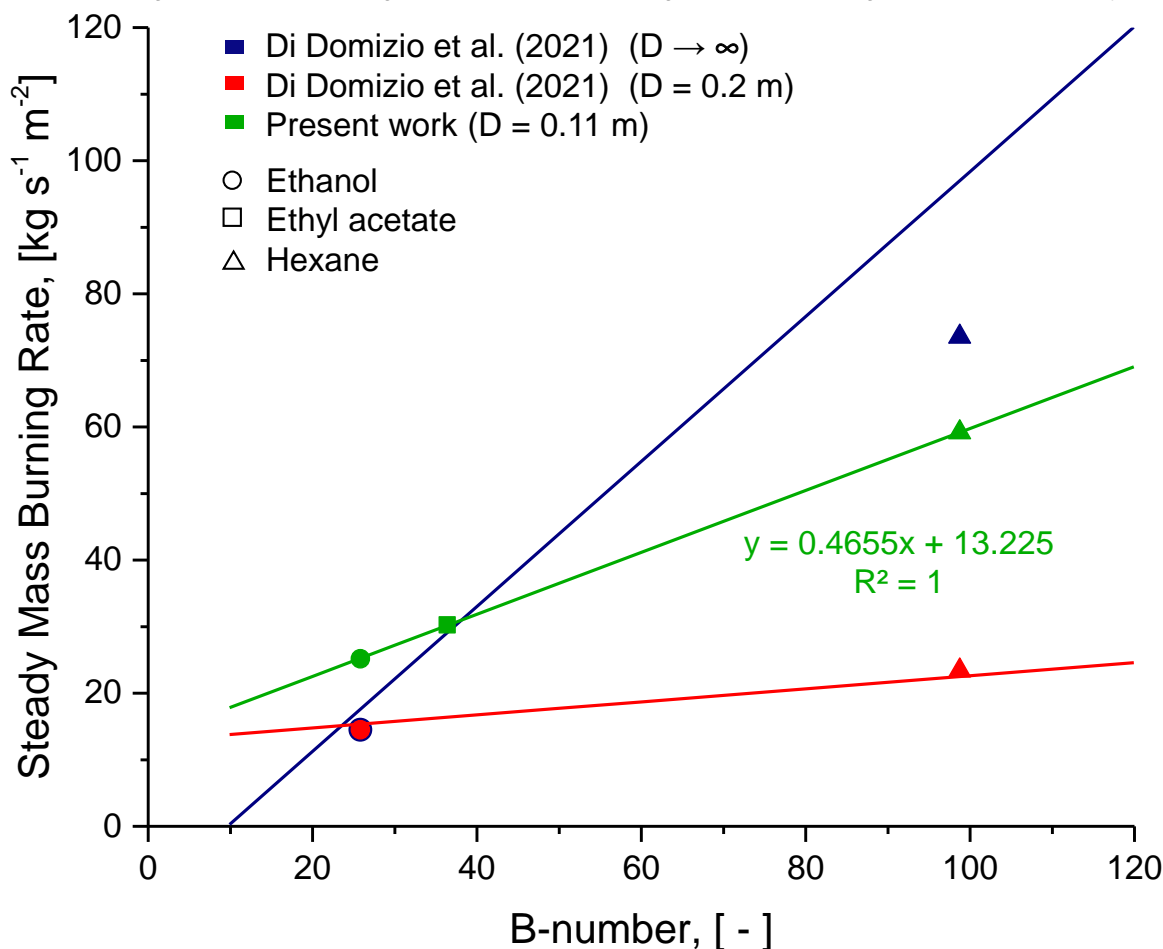


Figure 1: Comparison of the trends for the Mass Burning Rate based on newly collected measurements and data from the literature (DiDomizio et al., 2021) at different pool diameters (blue = infinitely large, red = 0.2 m, and green 0.11 m) obtained at 25 kW/m² as a function of B-number for ethanol (circle), ethyl acetate (square) and hexane (triangle).

4. Conclusions

This work presents an experimental investigation of the pool fires of three different species typically used in industrial processes as solvents or fuels, namely hexane, ethyl acetate, and ethanol. Different experimental conditions were tested at a bench scale monitoring the most relevant trends for the parameters representative of the energy and mass evolution within the time. This procedure allowed for the identification of a critical flux, i.e., the minimum external heat flux required to produce a stable and self-sustaining flame. The obtained values of critical flux are in line with the flash point trend. However, if typical parameters for the ignition time are considered, ethanol shows larger ignitability. Additional pieces of information were derived from the analysis of the combustion intensity and effectiveness at a steady-state regime. The obtained data indicate that hexane is more prone to partial oxidation than the other investigated species. Eventually, the effects of pool diameter on the mass burning rate were assessed by comparing the obtained data with experimental measurements and numerical predictions available in the current literature. The gathered information allowed for the definition of a set of boundary conditions and procedural steps to be considered for a robust and consistent analysis of liquid ignition and combustion at a bench scale.

References

- Babrauskas, V., 1983. Estimating large pool fire burning rates. *Fire Technol.* 19, 251–261.
- BS ISO 5660-1: 2015 + A1: 2019 — Reaction-to-fire tests — Heat release, smoke production and mass loss rate, 2019.
- Cameo, 2023. CAMEO Chemicals. Rep. CAMEO Chem. NOAA. URL <https://cameochemicals.noaa.gov/>. Access 09/2023.
- Chen, Y., Fang, J., Zhang, X., Miao, Y., Lin, Y., Tu, R., Hu, L., 2023. Pool fire dynamics: Principles, models and recent advances. *Prog. Energy Combust. Sci.* 95, 101070.
- Chen, Z., Wei, X., 2014. Analysis for combustion properties of crude oil pool fire. *Procedia Eng.* 84, 514–523.
- Chen, Z., Wei, X., Li, T., 2021. Experimental Investigation on Flame Characterization and Temperature Profile of Single/Multiple Pool Fire in Cross Wind. *J. Therm. Sci.* 30, 324–332.
- De Liso, B.A., Palma, V., Pio, G., Renda, S., Salzano, E., 2023. Extremely Low Temperatures for the Synthesis of Ethylene Oxide. *Ind. Eng. Chem. Res.* 62, 6943–6952.
- DiDomizio, M.J., Ibrahimli, V., Weckman, E.J., 2021. Testing of liquids with the cone calorimeter. *Fire Saf. J.* 126, 103449.
- DiDomizio, M.J., Weckman, E.J., 2016. An evaluation of methodologies for determining delay times in the cone calorimeter fire test. *J. Test. Eval.* 44, 1050–1063.
- Florit, F., Busini, V., Favrin, S., Rota, R., Derudi, M., 2022. Reaction Runaway as a Domino Effect of Pool Fire Engulfing an Ethoxylation Reactor. *Chem. Eng. Trans.* 91, 79–84.
- Gosse, A., 2000. BG Technologies Ltd., private communication.
- Hagen, B.C., Meyer, A.K., 2021. From smoldering to flaming fire: Different modes of transition. *Fire Saf. J.* 121.
- Hottel, H.C., 1959. Review of Certain Laws Governing Diffusive Burning of Liquids. *Fire Res. Abstr. Rev.* 1.
- Jenft, A., Collin, A., Boulet, P., Pianet, G., Breton, A., Muller, A., 2014. Experimental and numerical study of pool fire suppression using water mist. *Fire Saf. J.* 67, 1–12.
- Joulain, P., 1998. The behavior of pool fires: State of the art and new insights. *Symp. Combust.* 27, 2691–2706.
- Kolhe, A. V., Malwe, P.D., Chopkar, Y., Panchal, H., Ağbulut, Ü., Mubarak, N.M., Chowdhury, S., Amesho, K.T.T., 2023. Performance analysis of biofuel–ethanol blends in diesel engine and its validation with computational fluid dynamics. *Environ. Sci. Pollut. Res.* 30, 125117–125137.
- Liaw, H.J., Gerbaud, V., Chen, C.C., Shu, C.M., 2010. Effect of stirring on the safety of flammable liquid mixtures. *J. Hazard. Mater.* 177, 1093–1101
- Madani, S.S., Ziebert, C., Marzband, M., 2023. Thermal Characteristics and Safety Aspects of Lithium-Ion Batteries: An In-Depth Review. *Symmetry (Basel)*. 15.
- Malekshah, R.E., Moharramnejad, M., Gharanli, S., Shahi, M., Ehsani, A., Haribabu, J., Ouachtak, H., Mirtamizdoust, B., Kamwilaisak, K., Sillanpää, M., Erfani, H., 2023. MOFs as Versatile Catalysts: Synthesis Strategies and Applications in Value-Added Compound Production. *ACS Omega* 8, 31600–31619.
- Pio, G., Carboni, M., Iannaccone, T., Cozzani, V., Salzano, E., 2019a. Numerical simulation of small-scale pool fires of LNG. *J. Loss Prev. Process Ind.* 61, 82–88.
- Pio, G., Carboni, M., Salzano, E., 2019b. Realistic aviation fuel chemistry in computational fluid dynamics. *Fuel* 254, 115676.
- Pio, G., Dong, X., Salzano, E., Green, W.H., 2022. Automatically generated model for light alkene combustion. *Combust. Flame* 241.
- Quan, Y., Zhang, Z., Tanchak, R.N., Wang, Q., 2022. A review on cone calorimeter for assessment of flame-retarded polymer composites. *J. Therm. Anal. Calorim.* 147, 10209–10234.
- Rogers, R.L., 1996. Solvent flammability and reactivity hazards. *Dir. Solvents* 70–81.
- Stojadinović, D.J., Đorđević, A. V., Krstić, I.M., Radosavljević, J.M., 2023. Atmospheric release of organic solvents due to hazardous events in the paints and varnishes industry. *Hem. Ind.* 77, 111–127.
- Tahmid Islam, M., Klinger, J.L., Toufiq Reza, M., 2023. Evaluating combustion characteristics and combustion kinetics of corn stover-derived hydrochars by cone calorimeter. *Chem. Eng. J.* 452.
- Tarantola, G., Medri, E., Splendore, A., Lo Russo, F., Matteucci, C., Minelli, M., 2023. Liquid Foam-Ethyl Vinyl Acetate Adhesive Systems for Lining Process of Paintings: Prospects of a User-Friendly, Harmless Alternative to Conventional Products. *Polymers (Basel)*. 15.
- Uijt de Haag, P. A. M., & Ale, B.J.M., 2005. Guidelines for Quantitative Risk Assessment (Purple book).
- Vali, A., Nobes, D.S., Kostiuk, L.W., 2014. Transport phenomena within the liquid phase of a laboratory-scale circular methanol pool fire. *Combust. Flame* 161, 1076–1084.
- Van Wingerden, K., 2019. Mechanical sparks as an ignition source of gas and dust explosions. *Chem. Eng. Trans.* 77, 133–138.