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On the ignition hazards of combustible liquid: the case of S-lactic acid water solution

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ABSTRACT

The simultaneous exceedance of the flash point and the presence of an external source of ignition such as electrostatic sparks or hot spots lead to a flame-related scenario. Nevertheless, anomalous behaviour can be observed if the liquid is subject to thermal degradation, even below the flash point. This work is dedicated to the specific case of the hazard of combustible liquids due to the insurgence of secondary reactions activated by an ignition source and a constant heat flux to the sample within the range 7 kW/m^2 and 50 kW/m^2. To this aim, an aqueous solution having 90 %w lactic acid has been analysed experimentally by calorimetric analysis. The temperature of the liquid, the mass loss rate, and the heat release rate for the pool fire of lactic acid have been measured by a cone calorimeter. Results were compared with experimental data from the literature and theoretical data. The use of flash point temperature (regardless of the approach adopted for its evaluation) has been found to lead to non-conservative results on the safe side. Based on the collected data, the use of a cone calorimeter is recommended to evaluate the ignitability of liquid substances exposed to heating sources such as fires.

1. Introduction

Lactic acid or 2-hydroxy propanoic acid, $C_3H_6O_3$ (MW = 90.08 g/mol), is largely used in the pharmaceutical and food industry, showing a growing market because of its use as the renewable monomer for biodegradable polylactic acid (PLA) and polymers [1,2]. Its structure has a chiral carbon atom and two enantiomeric forms, the $S(+)$ lactic acid (S-LA, CAS 79-33-4), also defined as L-lactic acid and the $R(-)$ lactic acid (CAS 10326-41-7), or D-lactic acid (Fig. 1).

A literature review conducted by Ref. [3] indicates that the racemization of lactic acid occurs above 130 °C. Therefore, a complete characterization of thermochemical aspects involving each form is essential to properly deal with pure substances and mixtures of S-LA and R-LA. From a thermochemical point of view, the same Authors have reported a detailed analysis for S-LA, indicating the enthalpy of combustion as –1337.9 $\pm$ 0.8 $kJ\ mol^{-1}$ and standard heat of formation of 700 $\pm$ 0.9 $kJ\ mol^{-1}$. The enthalpy of vaporization is reported as 69.1 $kJ \pm 1.0\ mol^{-1}$, whereas the melting temperature is 57.25 °C. Slighly smaller absolute values of heat of formation and enthalpy of combustion are reported within the database published by the National Institute of Standards and Technologies [4]. Conversely, a dearth of data can be observed for R-LA, although a mixture of the two isomers is commercially available as DL-lactic acid or racemic lactic acid (DL-LA, CAS 50-21-5), where the two isomers are equimolar. The DL mixture is reported to melt at a lower temperature, about 16.8 °C, hence below the temperature of pure isomers. This temperature is often mistakenly addressed as the melting point of any isomer of lactic acid. For the DL-lactic acid [5], have shown the enthalpy of vaporization is – 56.90 $kJ\ mol^{-1}$. The boiling point of S-LA at atmospheric pressure is estimated to be 216.6 °C (QSAR calculation) by the European Chemicals Agency [6]. [7] reports the experimental data of Alfa Cesar at ambient pressure to be 267–271 °C.

Thermal analysis by DSC shows an intense endothermal peak starting at 174.2 °C, with negligible differences between S-LA and D-LA and a second peak which is attributed to the lactide formed by the dimerization of lactic acid. Besides, the DTG shows a first peak due to the evaporation of impurities typically present in lactic acid, mainly methanol, a second peak at 185.9 °C and a final peak related to lactide. In this regard, TG-MS curve profiles show many decomposition products when lactic acid is heated. At 300 °C, after heating for about 30 min, the dehydration to acrylic acid and the decomposition reaction to propionic acid and oxygen are observed. Since the start of heating, however, the

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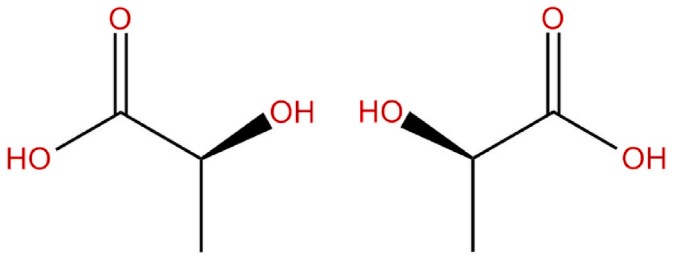

Fig. 1. The two isomers $S(+)$ (left) and $R(-)$ (right) lactic acid (2-hydroxypropanoic acid).

decarboxylation of lactic acid, with the formation of acetaldehyde and carbon dioxide (and hydrogen) is observed. Eventually [3], report a dimerization towards optically active lactide above 180°C. Indeed, the lactic acid self-reacts to lactides (lactone cyclic ester) on heating. Lactides are readily decomposed into fragments (carbon monoxide, acetaldehyde, and water) thus competing with the dehydration process to acrylic acid (Fig. 2).

From a safety standpoint, the flammability of liquids is often evaluated based on their flash point. In this context, the flash point is often intended as the lowest temperature at which a substance or a mixture emits enough vapour to form an ignitable mixture in air. This value can be derived from theoretical or experimental sources. Group contribution methods, estimations based on the chemical class, ab initio calculations, or kinetic mechanisms can be considered examples of theoretical approaches for the assessment of flash points, either for the assessment of the equilibrium composition in the vapour phase or flammability limits [8]. On the other hand, two main methodologies have been largely adopted for the experimental measurement of flash points, namely open cup and closed cup. The former reproduces an open environment where the liquid sample is gradually heated and ignition sources are periodically provided to the liquid-vapour interface, defining the flash point as the minimum temperature producing a momentaneous flame (but not sustained combustion) [9]. Conversely, the latter is based on a sealed cup, where a stirring mechanism guarantees homogeneous conditions within the closed environment and proper mixing with air during the controlled heating phase [10]. Also in this case, ignition sources are provided automatically at regular intervals. However, the sealed cup is momentarily opened to monitor the occurrence of ignition. In addition, the potential achievement of equilibrium composition within the sample holder generally leads to more conservative results on the safe side than the open cup approach. Several standards have been developed to this scope. Among the others, ASTM D93, ASTM D56, ASTM D92, ISO 2719, ISO 13736, EN ISO 3679, EN ISO 3680, and DIN 51755 are worth mentioning. In particular, ASTM D93 uses the Pensky-Martens closed cup method and is widely applied to measure the flash points of petroleum products, lubricants, and biodiesel. ASTM D56 employs the tag closed cup technique, which is best suited for low-viscosity, volatile liquids like solvents. ASTM D92 relies on the Cleveland open cup method, making it ideal for testing materials with higher flash points, such as lubricating oils. ISO 2719 mirrors ASTM D93 and also uses the Pensky-Martens closed cup, serving as an internationally recognised standard for flash point determination. ISO 13736 specifies the Abel closed cup method and is commonly used in Europe for evaluating the flash point of flammable liquids. EN ISO 3679 and EN ISO 3680 are European Norms that provide closed and open cup methods, respectively, and are typically used for paints, varnishes, and similar coating products. Eventually, DIN 51755 is a German standard frequently used within the EU regulatory environment for flash point testing. Further information on the subject, together with the elements to identify the most suitable approaches and correction procedures, can be retrieved in the dedicated literature [10,11] and technical documents [12]. It is worth noting that in both cases the investigated liquid is heated by conduction from the sample holder. However, in the case of accidental

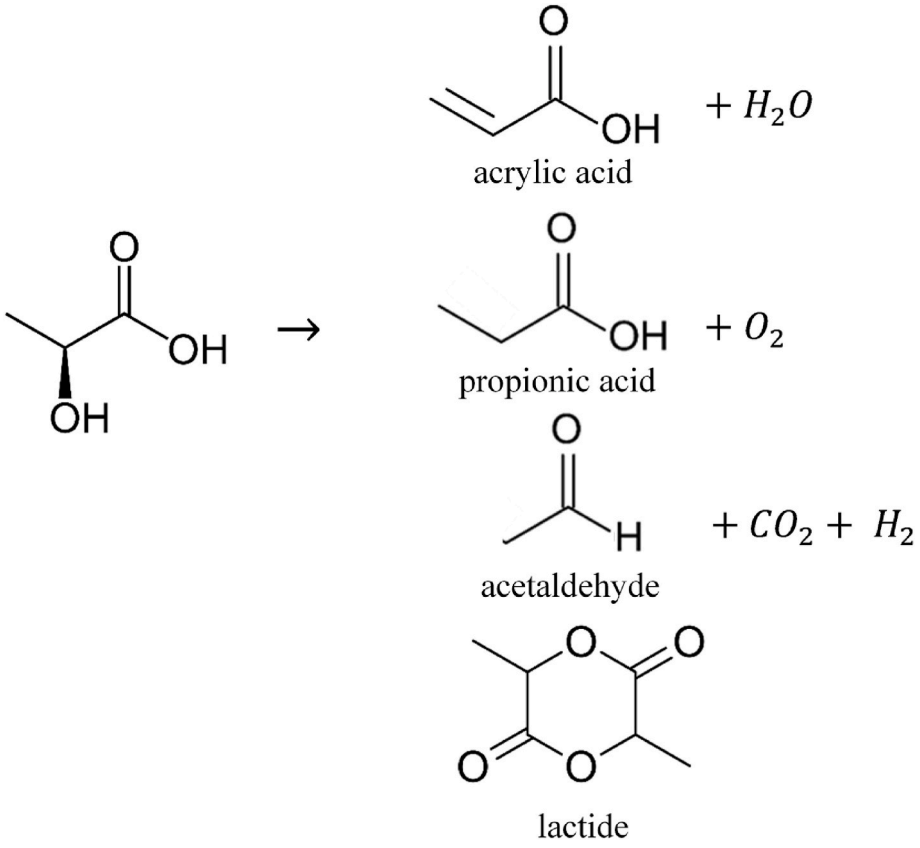

Fig. 2. The thermal degradation of lactic acid to acrylic acid, propionic acid, acetaldehyde and lactide (lactone cyclic ester).

release of liquids, heating sources can derive from surrounding fires. The presence of heat sources can also affect the composition of vapour because of the possible occurrence of pyrolysis and decomposition reactions.

It is worth mentioning that the current literature and the available MSDSs report a flash point for lactic acid between 110 °C [13] and 113 °C [14], which is a relatively high temperature if considering that the evaporation of lactic acid starts from the ambient temperature and the decomposition products (in particular acetaldehyde and carbon dioxide) are seen at very low temperature [5]. This aspect is particularly relevant considering the kinetics of combustion of acetaldehyde in air, as described in dedicated studies employing and validating detailed kinetic mechanisms [15]. Besides, the presence of water can play a significant role in the ignitability and flame intensity of organic species, based on the chemical structure and physical properties of the investigated compounds [16]. Here it is worth saying that ECHA, according to the ISO 3679:2022 [17], is not able to define a flash point for the 92 % water solution. Also, for the sake of this work, it is important to note that acrylic acid, propionic acid and acetaldehyde have a flash point of 68 °C, 54 °C and −38 °C, respectively. Eventually, the auto-ignition temperature (AIT) of lactic acid is considered $\geq$ 400 °C, according to ECHA. However, the AIT of acetaldehyde (175 °C), acrylic acid (429 °C) and propionic acid (512 °C) should be of concern.

To properly characterize the ignitability under these circumstances, alternative solutions are needed. Recently, the convenience in using a set of data derived from cone calorimeter tests to quantify the most relevant safety parameters of liquid substances exposed to thermal and electric energy sources has been presented, including the possibility of integrating experimental results with advanced numerical features [18]. Hence, considering the target scenario and mixture, a cone calorimeter represents a promising solution, especially for the characterization of components involved in electrochemical systems [19]. Indeed, a conical-shaped radiant heater is designed to emit a controlled heat flux toward a square-based sample, simulating a fire as a heat source, whereas a controlled spark ignition can be provided to investigate the combined effects of thermal and electric energies on degradation and ignitability of materials. This system is able to characterize bench-scale samples, monitoring the mass, temperature, and emitted power of the tested materials as well as the composition and flowrate of the exhaust gas produced during the pyrolysis and combustion processes. More specifically, measuring systems within the exhaust hood aim to characterize the composition as well as the released heat power, whereas the mass of the sample is monitored to assess the consumption rate [20]. Additional information on the constituting elements and the standard procedure can be retrieved in the dedicated literature [20–22]. This bench-scale instrument is widely employed in fire science to assess the flammability of solid materials. Nevertheless, the principles behind its design do not limit the application to solid materials, as demonstrated by DiDomizio et al. (2021) [23] who have proposed a methodology for the evaluation of liquid samples through a cone calorimeter. More recently, this approach has been further developed to assess the ignitability in the presence of an electric spark [24] under a wide range of conditions.

For these reasons, an experimental campaign devoted to the characterization of the ignition behaviour of lactic acid was conducted in this work through bench-scale calorimetry (cone calorimetry) tests.

2. Methodology

Aqueous solution of S-LA lactic acid (90 %w) (Titolchimica SpA) has been tested in this work. The liquid was added to a parallelepipedal sample holder having a square base of $L = 10\ cm$ and a thickness of 2 cm. Samples were exposed to constant external heat fluxes of 7, 25, 35, and 50 kW/m^2. The external fluxes were guaranteed by keeping a conical shape resistance at a specific constant temperature, as reported in Table 1.

To assess the potential for electrostatic ignition, two cases were examined: (1) a 10 kV spark was applied at the liquid-vapour interface at 60-s intervals, and (2) no external ignition source was provided during the tests. This approach allowed for the evaluation of both the presence and absence of electrostatic ignition conditions. In both cases, the exhaust composition, temperature, and pressure during each test were monitored. A load cell was adopted to measure the time evolution of the mass of the sample. The adopted experimental system is reported in Fig. 3, and described in detail elsewhere [25].

Table 1
External heat flux provided to the sample and the corresponding temperature of the cone (T_{cone}).

Heat flux [kW/m^2]	T_{cone} [K]
7	680
15	756
25	877
35	956
50	1045

Based on the measured data, several physical and chemical properties were obtained, including the heat release rate (*HRR*), the effective heat of combustion (*EHC*), and the mass loss rate (MLR). More specifically, the *HRR* is calculated based on oxygen depletion, in compliance with the methodology described within the ASTM E 1354/ISO 5660 standards [21], the *EHC* is intended as the amount of heat released per unit mass of material consumed during the test, and the *MLR* is measured as the first derivative of the measure sample mass to time. Therefore, the *EHC* can be compared with theoretical or empirical derived values of heat of reaction to identify the most relevant steps during the decomposition phenomena. The amount of oxygen, carbon monoxide, and carbon dioxide within the gaseous stream has been detected by paramagnetic and IR analysers, whereas a laser photometer beam (He-Ne beam) has been adopted for a qualitative assessment of the presence of particulate matter.

The methodology for the evaluation of the enthalpy of combustion adopted in this work follows the concept of the standard behaviour of the *EHC* with time, which shows a plateau when the combustion of the pool is fully developed after the transient regime of the post-ignition conditions. This plateau does not depend on the heating system and is generally more evident for low heating power. However, total oxidation to CO_2 is only obtained if correction for the partial oxidation to *CO* is considered, hence, the *EHC* is corrected by the energy produced by the oxidation of *CO* to CO_2.

3. Results and discussion

The following Fig. 4 gives the experimental measurement for the S-LA as obtained in a cone calorimeter by using a spark ignition (Fig. 4) with an interval of 60 s. The heating power varies between 7 kW/m^2 and 50 kW/m^2.

From the reported data, it is clear that, once exposed to 7 kW/m^2, the specimen evaporates slowly and, despite the presence of the high-energy spark ignition, no pool fire or stable flames can be observed. Increasing the external heat flux to 25 kW/m^2 and 35 kW/m^2, a significant variation in the mass loss rate due to evaporation is clearly detected at 300 s and 120 s, respectively. At that point, a combustion phenomenon starts after ignition, as supported by the observed production of CO_2 ($\geq 200\ mg/s$) and heating power. At 25 kW/m^2, a plateau of *EHC* for about 2 min at $12.84 \pm 0.33\ MJ/kg$ is observed. If corrected for the CO oxidation, this value is about $-14.85\ MJ/kg$ (or $13.38\ MJ/mol$), which corresponds to the direct measurements reported in the literature [3]. At 35 kW/m^2, the achievement of a constant value for EHC is less evident and ranges for about 1 *min* at 10.5 MJ/kg. However, if corrected for the *CO* oxidation, this value returns to be 13.38 MJ/mol. Similar considerations can be made for the 50 kW/m^2.

The temperature of the on-set of the combustion is very low in all

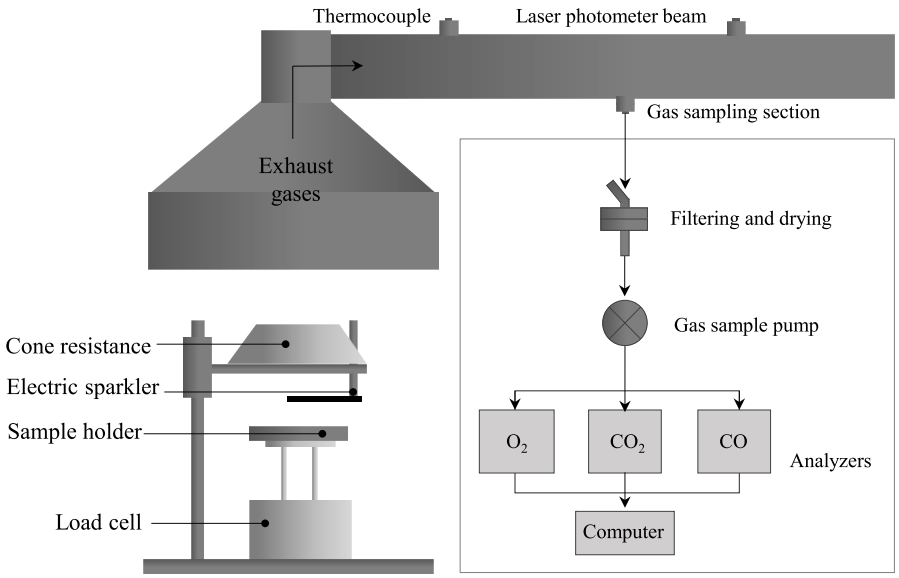

Fig. 3. Overall schematic configuration of cone calorimeter apparatus.

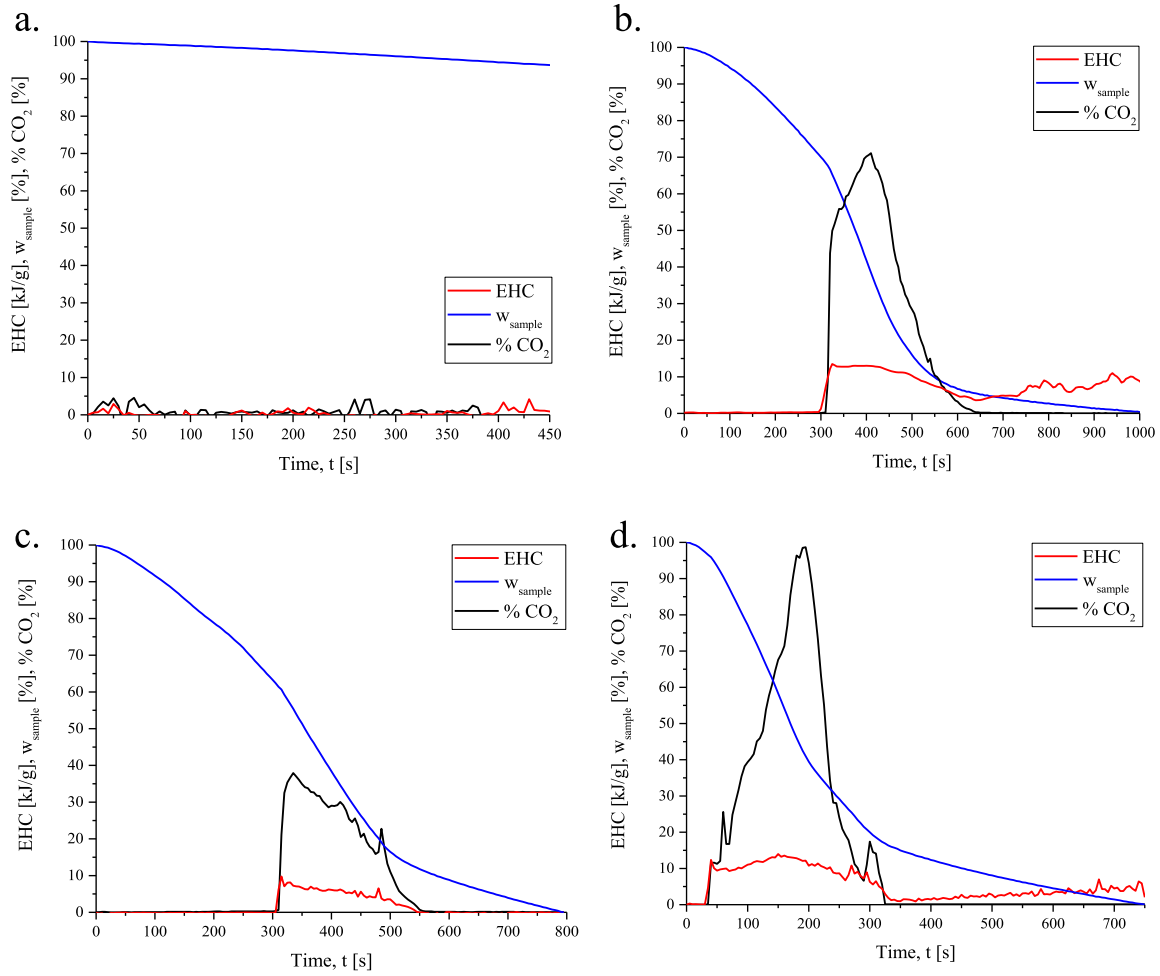

Fig. 4. The time evolution of the temperature, the mass of the specimen, the Effective Heat of Combustion, and the CO_2 percentage measured during the exposition of S-lactic acid at a constant heat flux of 7 kW/m^2 (a.), 25 kW/m^2 (b.), 35 kW/m^2 (c.) and 50 kW/m^2 (d.) in the presence of a temporized ignition source.

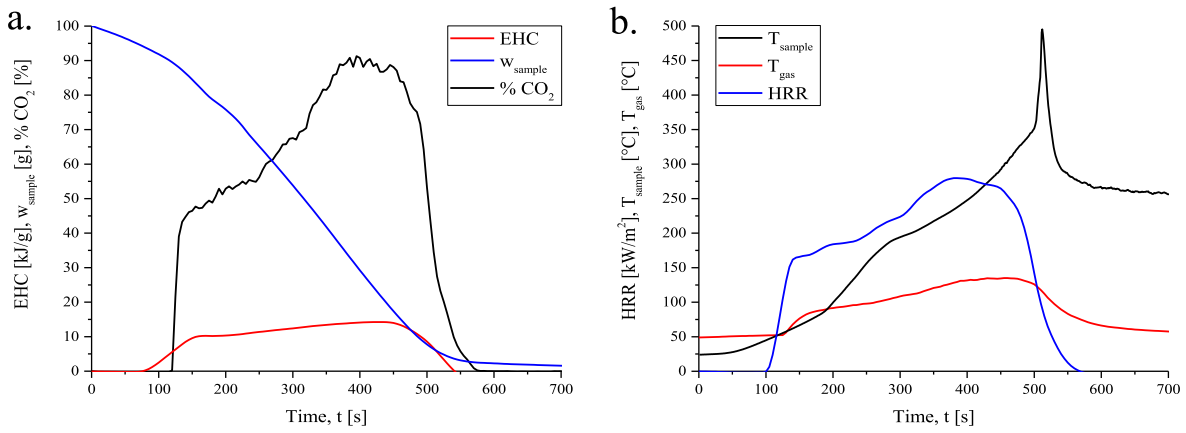

Fig. 5. The time evolution of the mass of the specimen, the Effective Heat of Combustion, and the CO_2 percentage measured during the exposition of S-lactic acid at a constant heat flux of 35 kW/m^2, in the presence of a temporized ignition source (a) and the Heat Release Rate, the temperature of the sample and the temperature of the gas phase over time during the same test. The initial mass of the specimen is 75 g.

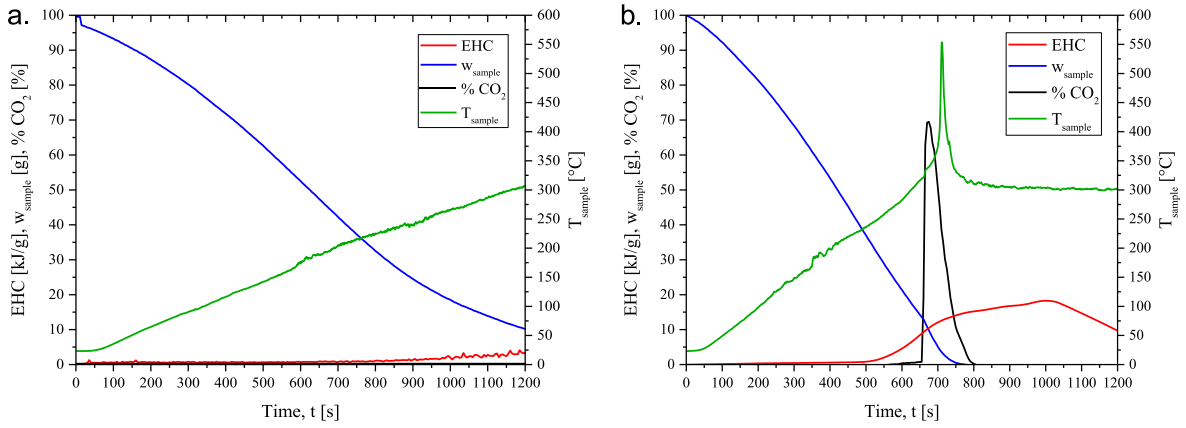

Fig. 6. The time evolution of the temperature and the mass of the specimen, the Effective Heat of Combustion, and the CO_2 percentage measured during the exposition of S-lactic acid at a constant heat flux of 25 kW/m^2(a) and 35 kW/m^2(b), in the absence of an ignition source.

cases, at about 26 °C. Hence, a possible explanation can be attributed to the occurrence of decomposition reactions within the vapour phase, leading to the production of more flammable substances, such as acetaldehyde. Under this hypothesis, the use of flash point as a standalone parameter is discouraged, whereas a complete characterisation accounting for the possible decomposition reaction is recommended, especially for organic compounds where decomposition products may have more tendency to ignite than the initial compound. To support this assumption, another test has been performed with a different initial mass (i.e., 75 g) and the same external heat flux to the sample. Results are reported in Fig. 5. Also in this case, the ignition at low temperature is confirmed and the measured temperature is lower than the flash point of lactic acid for the entire duration of the test. Referring to the Heat Release Rate profile (*HRR*, panel b.), after a pre-heating phase of around 100 s, an abrupt increase marks the onset of the combustion process. Then, a slower rise in the HRR is observed, characterized by a fully developed flame. The peak of the power production is reached after around 400 s, followed by a quasi-stationary phase. The HRR gradually decreases as the fuel is almost consumed, indicating the end of the combustion mechanism.

The following Fig. 6 provides the experimental measurements for the S-LA as obtained in a cone calorimeter without the use of a spark ignition and heating power of 25 W/m^2 and 35 W/m^2.

The comparison of the time evolution of specimen mass and liquid temperatures shows similar results for the reported conditions. The temperature of the liquid is below the flash point for the entire duration of the test. However, from the measured flowrate of produced CO_2, it is possible to infer that only at 25 kW/m^2 no combustion is observed in the absence of spark ignition. Indeed, at 35 kW/m^2 the mass loss is constant (evaporation) up to 650 s, where shreds of evidence of combustion phenomena can be noted, e.g., significant production of CO_2, (about 25 %).

The ignition delay can be associated with the temperature and composition of the vapour phase. Indeed, contact with the hot surface of the radiative element can guarantee the achievement of the minimum ignition temperature (either for lactic acid, acetaldehyde or acrylic acid) only once the external flux exceeds 35 kW/m^2. Hence, it is possible to conclude that the evaluation of safety aspects based on the properties of the initial liquid can produce non-conservative results in the case of scenarios having a heat source in the proximity of the investigated species. These discrepancies can be attributed to the partial decomposition toward lighter and more flammable species in the vapour phase. Besides, the thermal power produced by the combustion shows a plateau for about 2 min at 13.8 MJ/kg, which is slightly higher than the value obtained in the presence of a spark ignition, possibly due to the effect of thermal radiation.

4. Conclusions

The presence of heat radiation or an electric spark can dramatically affect the chemical structure and the combustibility of the liquid mixtures containing lactic acid, making the flash point value reported in the

literature not representative of safety evaluations. The possible explanation is related to the formation of thermal decomposition products (acetaldehyde and acrylic acid), which are extremely flammable at low temperatures. This aspect is particularly relevant in the view of the ignition phenomena. Indeed, it is unlikely that a small static spark can vaporise water or directly decompose lactic acid, which is expected to be almost inert at moderate conditions. While low-energy sparks might ignite these volatile by-products, supporting the realisation of a stable flame at milder temperatures. Therefore, the use of a cone calorimeter test is suggested for the characterization of safety parameters of liquids once the ignition in the proximity of a heat source is of concern.

CRediT authorship contribution statement

B.A. De Liso: Writing – original draft, Investigation, Formal analysis, Data curation. **G. Pio:** Writing – review & editing, Supervision, Methodology, Conceptualization. **E. Salzano:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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