

Explosion Characterization of Solid Lactic Acid

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Lactic acid (LA) is a molecule of significant industrial interest, utilized in various sectors. In the food industry, it is used as a preservative and pH regulator in baked goods, dairy products, and beverages. Additionally, it finds applications in the pharmaceutical industry, where it is used in skincare creams, chemical peels, and as a moisturizing agent. Furthermore, lactic acid is employed in the chemical and textile industries. Conversely, to poly-lactic acid (PLA), its explosiveness and thermodynamic properties are not well-documented in the scientific literature. Indeed, only a few relevant works provide a comprehensive overview of lactic acid properties, applications, and production. However, such reviews neither specifically address the explosiveness of lactic acid nor study its thermodynamic properties, providing valuable data on either its thermal stability or behavior at different temperatures and pressures. This work aims at bridging these lacks by exploring LA (here considered as a racemic mixture of either L or D-lactic acid) thermochemical behavior (through thermogravimetric studies and modelling), explosive potential (calculating either Minimum Ignition Energy, MIE, or Deflagration Index, K_{st}), and associated safety challenges. Through this work, the authors also wish to provide a foundation for both enhancing industrial safety and unlocking new applications for this versatile compound.

1. Introduction

Lactic acid (LA) is a multifunctional compound with wide industrial applications due to its relevant physicochemical properties, such as mild acidity, hydrophilic nature, and compatibility with a wide range of substances. This versatility has made it indispensable for several industrial applications, ranging from food preservation to pharmaceutical formulations and biodegradable polymers (Castillo Martinez et al., 2013). Particularly, it is used as a pH regulator and stabilizing agent in baked goods, dairy products, and beverages; in fact, its ability to inhibit microbial growth ensures extended shelf life for various products (Eş et al., 2018). Moreover, LA finds a prominent role in the pharmaceutical and cosmetic sectors due to its biocompatibility and moisturizing properties (Wang et al., 2016). In the chemical industry, LA is used either as a precursor in synthesizing biodegradable polymers or as a valuable intermediate in chemical reactions (Yu et al., 2023). In textiles, LA finds applications as a finishing agent in dyeing processes because its role as a pH regulator ensures both dye stability and better binding to fabrics. Additionally, its biodegradability aligns with the growing demand for eco-friendly practices in the textile sector.

Recent advancements have explored the potential of LA in innovative fields, such as biomedical engineering (LA-based polymers are investigated for both tissue engineering and bioresorbable medical devices), green chemistry (the use of LA as a feedstock for synthesizing other biodegradable and bio-based chemicals, such as lactate esters, highlights its role in sustainable chemical manufacturing) and agriculture (LA serves as a component in eco-friendly fertilizers and pesticides, emphasizing its utility in sustainable farming practices). Finally, it is possible to state that the global lactic acid market is expanding rapidly, driven by the increasing demand for biodegradable materials and eco-friendly solutions. Lactic acid, with its non-toxic and biodegradable properties, is at the forefront of this growth. Its adoption aligns with international environmental goals, such as reducing reliance on petrochemicals and enhancing industrial sustainability (Nazer et al., 2021).

Concluding this introductory overview, while the applications of LA are well-documented, the understanding of its explosiveness and thermochemical behavior remains fragmented. Studies by Emel'yanenko et al. (2010) on L-LA have provided foundational data. From a thermochemical point of view, they have indicated an enthalpy of combustion of -1337.9 ± 0.8 kJ/mol and a standard heat of formation of 700 ± 0.9 kJ/mol. The enthalpy of vaporization has been reported equal to 69.1 ± 1.0 kJ/mol, whereas the melting temperature has been found equal to 57.25 °C. On the contrary, a dearth of data can be observed for D-LA, which is quite difficult (also because of the associated costs) to separate from its enantiomer. Generally, the most diffused form of commercial LA is a 1:1 (w:w) mixture of the two isomers, known as DL-lactic acid or racemic lactic acid (DL-LA, CAS 50-21-5). The DL mixture is reported to melt at a lower temperature with respect to the pure isomers, which is about 16.8 °C. Unfortunately, this temperature is often addressed as the melting point of any isomer of lactic acid, making some confusing data.

For the DL-lactic acid, Komesu et al. (2017) have shown that the enthalpy of vaporization is around -56.90 kJ/mol. Their thermal analysis by DSC has shown an intense endothermic peak starting at 174.2 °C, with negligible differences between S-LA and D-LA, and a second peak (at 352 °C) which could be attributed to lactide, which is a compound formed by the dimerization of lactic acid. Besides, the DTG graph has shown a first peak due to the evaporation of impurities typically present in lactic acid, mainly methanol, a second peak (at 185.9 °C) of dubious entity, and a final peak related to the lactide formation. In this regard, TG-MS curve profiles have shown many decomposition products when lactic acid is heated. At 300 °C, the dehydration to acrylic acid and the decomposition reaction to propionic acid and oxygen have been observed. Since the start of heating, however, the decarboxylation of lactic acid, with the formation of acetaldehyde and carbon dioxide (and hydrogen) has been also observed. Finally, Emel'yanenko et al. (2010) report a dimerization towards optically active lactide (lactone cyclic ester) only above 180 °C. Indeed, the lactic acid self-reacts to lactides on heating. Lactides are readily decomposed into fragments (carbon monoxide, acetaldehyde, and water) thus competing with the dehydration process to acrylic acid.

Eventually, it is worth saying that, besides these studies, no data related to either flammability (e.g. Flash Point, Lower and Upper Flammability Limits, etc.) or explosibility (e.g. Minimum Ignition Energy, Deflagration Index, etc.) of lactic acid are currently available in the scientific literature. This work aims at proposing a theoretical approach which, based on already available thermochemical data, can provide some of this missing information with a quite high degree of accuracy.

2. Theoretical Models

In the following, the mathematical models used to estimate Minimum Ignition Energy (MIE), Flash Point (FP) and Deflagration Index (K_{st}) will be presented. It is worth noting that the complete theoretical background of all these models has been already detailed in previous literature works; therefore, within this paper, they will be only briefly summarized (highlighting the main hypotheses on which they are based).

2.1 The estimation of Minimum Ignition Energy and Flash Point

The Minimum Ignition Energy (MIE) is either a flammability or explosibility parameter used to characterize gases, liquids and solids (in the form of dust suspension). When referred to dust, it is usually evaluated using the MIKE3 equipment (see Hartmann tube design), according to different standard procedures; in particular, in this work, the standard procedure EN ISO/IEC 80079-20-2:2016 was referred to. Otherwise, the Flash Point (FP) is a flammability parameter used to characterize mainly liquids rather than solids; it is usually measured in a Pensky-Martens' apparatus (using a closed cup test) referring to the UNI EN ISO 2719:2021 standard.

To estimate the value of either MIE or FP for DL-LA, the mathematical model reported in the work of Copelli et al. (2021) was used. Particularly, the following hypotheses were applied:

- 1) LA was considered as either solid (for MIE determination) or liquid (for FP estimation) particles of spherical shape (different mean diameters - 50 , 100 and 150 μm – were investigated);
- 2) the devolatilization kinetics of the solid/liquid particles was fitted using thermogravimetric (TG) data reported in the work of Komesu et al. (2017), with particular reference to a heating rate of 5 K/min (the lowest available);
- 3) the Lower and Upper Flammability Limits for LA volatile compounds were assumed to be equal to those of methanol (that is, $6.7 - 36$ % v/v), as it was indicated as one of the major contaminants in the analyzed sample of LA (or, at least, the first compound emitted in the gaseous phase during the devolatilization phenomenon);
- 4) the vaporization enthalpy of LA was assumed equal to 69.1 kJ/mol, as reported by Emel'yanenko et al. (2010);
- 5) the geometry of the simulated system was referred to as a MIKE3 apparatus (1.2 L of overall volume);

- 6) the following correlation for MIE calculation was used (basing on 5 tests per level of energy virtually tested, that is one per solid mass loaded into the simulated MIKE3 apparatus: 300, 600, 900, 1200 and 1500 mg, respectively):

$$MIE = 10^{\left(\log_{10}(E2) - \left(I[E2] \cdot \frac{\log_{10}(E2) - \log_{10}(E1)}{(NI+I)[E2]+1}\right)\right)} \quad (1)$$

where: $E2$ is the minimum ignition energy at which the ignition occurs [mJ], $E1$ is the maximum ignition energy at which the ignition always fails [mJ], $I[E2]$ is the number of tests at $E2$ in correspondence of which the ignition occurs [-] and, $(NI + I)[E2]$ is the total number of tests done at the energy level $E2$ [-].

- 7) the temperature in the hot core zone in correspondence of the calculated MIE value (Eq. (1)) for LA particles of diameter equal to 50 μm (750 mg loaded – to be as closest as possible to the Pensky-Martens conditions for FP test) was assumed as a good estimation of the LA Flash Point (to be compared with a literature value to validate the proposed approach).

2.2 Estimation of the Deflagration Index

Deflagration Index (K_{st}) is an explosibility parameter usually determined using a 20 L sphere apparatus referring, as the sake of example, to the ISO 6184/1 standard.

To estimate the value of the K_{st} for LA, the mathematical model reported in the work of Copelli et al. (2019) was used. The first four hypotheses applied were the same as those ones previously reported in paragraph 2.1 for MIE estimation; but the following needed to be added to:

- 1) the geometry of the simulated system was referred to as a 20 L sphere apparatus (Siwek chamber);
- 2) the deflagration index was calculated using its definition, that is:

$$K_{st} = \left(\frac{dP}{dt}\right)_{max} \cdot V^{\frac{1}{3}} \quad (2)$$

where: $\left(\frac{dP}{dt}\right)_{max}$ is the maximum rate of pressure rise in the 20 L sphere [bar/s] and V is the volume of the sphere used for the test [m^3];

- 3) the derivative of pressure with respect to time was directly calculated by the temperature derivative provided by the model using the ideal gas law (which was assumed to be valid for describing the gas phase behavior inside the sphere).

3. Results and Discussion

In the following the results obtained by the theoretical simulations for the determination of Minimum Ignition Energy, Flash Point and Deflagration Index of lactic acid will be presented and discussed.

3.1 Fitting of the TGA curve

As described in the work of Copelli et al. (2021), the devolatilization kinetics of any organic compound can be determined by a suitable fitting of thermogravimetric (TG) data (provided in the format of mass loss – or conversion – vs. temperature), considering four different parameters: A (which is the classical pre-exponential factor of an Arrhenius kinetic constant), E_{att} (which is the activation energy), k (which is a corrective factor for activation energy, taking into account the modification of the decomposing mixture composition during the devolatilization process) and, n (which is the apparent reaction order). According to hypothesis 2) of paragraph 2.1, TG data were taken by the work of Komesu et al. (2017).

Figure 1 reports both the experimental data and the best fit (for the first part of the curve). As it is possible to observe, the overlapping of the two conversions vs. temperature curves is very good in the first temperature range (before 100 °C), becoming less accurate as the temperature increases. This is in line with the procedure detailed in Copelli et al. (2021), where the first part of the curve, describing the earliest volatiles produced by either pyrolysis or devolatilization of the condensed substance to be tested, were the most important to calculate the value of either the MIE or the K_{st} .

The results of the fitting procedure (that is, all the four kinetic parameters) are reported in Table 1.

3.2 Minimum Ignition Energy and Flash Point

In order to consider LA in the solid state (that is, as a dust), it was necessary to start the virtual MIKE3 test at the initial dust temperature of 0 °C (as the reported literature melting point of the racemic mixture was 16.8 °C).

Table 2 reports MIE results using three different mean diameters for the solid lactic acid particles, that were: 50, 100 and, 150 μm . These values were found to be the most likely for LA dust, but further experimental validation should be provided basing on real samples of crystalline lactic acid.

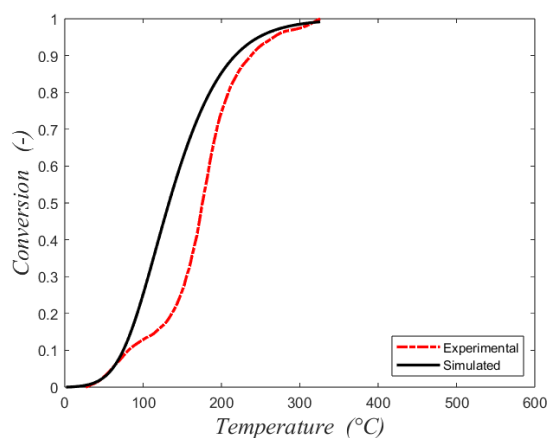


Figure 1: Conversion vs. Temperature curve for both the TG test at 5 K/min reported in Komesu et al. (2017) (red dotted line) and the simulated one (black continuous line) using the kinetics reported in Table 1.

Table 1: Kinetic parameters for the devolatilization kinetics

Parameter	Value	Unit
A	8.590×10^4	$1/s (kmol/m^3)^{1-n}$
E_{att}	5.108×10^4	J/mol
k	-0.152	-
n	2	-

Table 2: Theoretical MIE values for different mean diameters of solid LA.

Diameter [μm]	MIE [mJ]
50	0.81
100	8.52
150	430.68

All MIE values were calculated using Eq. (1), according to the results (for energy levels E1 and E2) of the simulations synthetically reported in Table 3 (as a function of the different solid LA masses virtually tested per each mean diameter of the dust). As it is possible to observe from the MIE values, when the dust mean diameter is little (ref. 50 μm), solid LA volatilized very easily, behaving more as a flammable liquid or gas rather than a powder. This could be ascribed to the fast evaporation of flammable contaminants (such as methanol) followed by a rapid devolatilization of the remaining matrix in either the liquid or the solid form. Therefore, the MIE value is very low in comparison with other dusts of the same particle size (e.g. sugar). As the mean particle dimension increases, LA seems to become lesser flammable (e.g., when the diameter is above 150 μm , the expected MIE value is quite high).

Concerning the estimation of the Flash Point, it is possible to refer to the temperature of the “hot zone” inside a MIKE3 apparatus, as described in Copelli et al. (2021). The temperature reached by the gas in the space between the electrodes depends on the energy released by the electrodes themselves and it can be used to model both the heating of the LA droplets and their vaporization rate. An ignition (that is, a flame) can result only when the concentration of volatile flammable compounds in the “hot zone” is inside the flammability limits (which must be known, at least for one of the expected emitted compounds). This means that the “hot core” temperature is somewhat linked to the flash point. Of course, quite small liquid droplets must be used for the virtual FP simulation because LA must vaporize rapidly when heated.

Moreover, the initial droplet temperature should be higher than 16.8 $^{\circ}\text{C}$, which is the melting point of DL-LA (for which the devolatilization kinetics was calculated); in this work, an initial droplet temperature of 20 $^{\circ}\text{C}$ was assumed. Finally, a surface/volume ratio similar to that one available in a standard Pensky-Martens apparatus should be used to ensure a good degree of reliability in the FP estimation.

Taking into account all of these constraints, the calculated FP was 105.5 °C. For DL-LA, Sigma-Aldrich's safety datasheet reports a value equal to 113 °C (closed cup test). This good agreement with the experimental result can be considered as a preliminary validation even of the LA data coming from the MIE model (which, of course, it has been already validated with other organic dusts such as sugar, niacin, aspirin, etc..) and a good premise for the use of the deflagration index model (which is based on the same devolatilization kinetics of the MIE model). Of course, a certain degree of uncertainty is unavoidable. Typically, it is possible to assume a 20% degree of uncertainty on the predicted MIE results.

Table 3: Results of E2 and E1 as a function of solid LA mass (mean diameters 50, 100 and 150 μm) loaded in the MIKE3 apparatus.

Ignition Energy [mJ]	Dust Loading 1,2 L chamber [mg]					
	300	600	900	1200	1500	
D=50 μm						
E2 = 3	I	I	I	I	I	
E1 = 0.007	NI	NI	NI	NI	NI	
D=100 μm						
E2 = 9	NI	NI	I	I	I	
E1 = 1	NI	NI	NI	NI	NI	
D=150 μm						
E2 = 431	NI	NI	I	I	I	
E1 = 99	NI	NI	NI	NI	NI	

3.3 Deflagration Index, K_{st}

The deflagration index was calculated based on the first four hypotheses of paragraph 2.1 and those of paragraph 2.2. Figure 2 reports the trend of the K_{st} as the function of the mean tested diameter of the hypothetical solid LA particles.

As already detailed for MIE estimations, the predicted K_{st} values are subjected to a certain degree of uncertainty. In this case a 20% uncertainty was taken into account as error bars on ordinates in Figure 2.

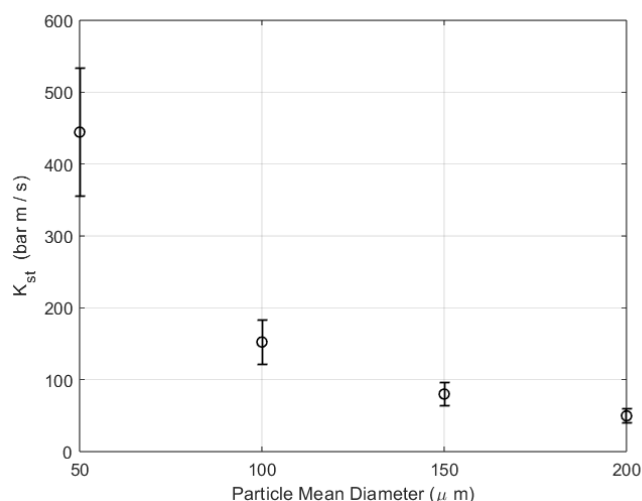


Figure 2: K_{st} as the function of the mean diameter of the LA particles.

As it is possible to notice, the value of the Deflagration Index decreases rapidly as a function of the mean diameter of the solid LA particles. This behavior is in line with that one observed for the MIE (which conversely increased): when LA particles are very little (that is, below 60 μm) they exhibit a gas-like behavior even in terms of either flammability or explosibility; otherwise, when the mean characteristic dimension increases, LA tends to

behave as a dust particle. Moreover, it is interesting to highlight that with particle size above 200 μm LA cannot be considered as explosible anymore.

4. Conclusion

Solid lactic acid (in its DL racemic form) is a versatile and valuable compound with widespread applications in the food, pharmaceutical, chemical, and textile industries. Its significance is amplified by its role in producing biodegradable materials like poly(lactic acid) and its alignment with sustainability goals. However, despite its industrial prominence, several critical gaps in understanding its safety profile, mainly its flammability and explosivity behavior, can be traced.

Particularly, no information on both the Minimum Ignition Energy and the Deflagration Index for lactic acid in its crystalline form can be found in the scientific literature.

Therefore, using already scientific literature available mathematical models, both MIE and K_{st} values were calculated for DL-LA in its solid crystalline form. From the results, it was possible to observe that for low particle size (that is, below 60 μm) LA behaves as a flammable liquid/gas, exhibiting low MIE and high K_{st} values. Increasing the mean diameter, LA started to behave as a dust, showing quite high MIE and low K_{st} values (quite close to those of either a common wheat flour or a sugar used for bakery purposes).

A partial validation of the reliability of these theoretical predictions was done by a good comparison between the calculated (using the same devolatilization kinetics used for both MIE and K_{st} calculations) and experimental flash point value. Anyway, a complete experimental characterization of solid LA flammability and explosibility should be done to complete its safety characterization, fundamental for process safety purposes.

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