



Synergistic behavior of flammable dust mixtures: A novel classification

Luigi Centrella^a, Maria Portarapillo^{b,*}, Giuseppina Luciani^b, Roberto Sanchirico^a,
Almerinda Di Benedetto^b

^a Istituto di Ricerche sulla Combustione - Consiglio Nazionale delle Ricerche (IRC-CNR), Piazzale V. Tecchio 80, 80125, Napoli, Italy

^b Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125, Napoli, Italy



GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: G. Lyberatos

Keywords:

Process safety
Dust flammability
Synergistic behavior
Dust mixtures classification

ABSTRACT

In this work the flammable/explosive behavior of mixtures of flammable dusts is investigated. In particular, minimum ignition temperature, minimum ignition energy, maximum pressure and deflagration index have been measured at varying the relative content of dusts in the mixtures. The thermal behavior of these mixtures has been also studied by means of DSC analysis coupled to chemical analysis performed by HPLC and ATR-FTIR.

Depending on the mixtures, a synergistic behavior has been found due to physical and/or chemical reactions. For some mixtures, the more severe behavior has been attributed to the presence of a eutectic point (niacin/anthraquinone, ascorbic acid/niacin), in other cases, to chemical reactions with the formation of volatiles (ascorbic acid/irganox 1222, ascorbic acid/glucose).

On this basis, we propose a new classification of dusts mixtures in three mixtures safety classes (MSC): MSC 0 (no synergistic effect, ideal behavior); MSC 1 (deviation from ideality, safety parameters included between those of the pure dusts) and MSC 2 (at least 1 parameter with more severe value than those of pure dusts).

1. Introduction

In many industrial chemical processes, mainly pharmaceutical and food industries, mixtures of flammable dusts and hybrid mixtures are often encountered.

As in the case of pure dusts, prevention and mitigation measures

have to be designed on the basis of the evaluation of flammability and explosion parameters.

In order to classify the flammability of dusts, the evaluation of the minimum explosive concentration (MEC), the limiting oxygen concentration (LOC), the minimum ignition temperature (MIT) and the minimum ignition energy (MIE) is required.

* Corresponding author.

E-mail address: maria.portarapillo@unina.it (M. Portarapillo).

<https://doi.org/10.1016/j.jhazmat.2020.122784>

Received 22 January 2020; Received in revised form 17 April 2020; Accepted 18 April 2020

Available online 30 April 2020

0304-3894/ © 2020 Elsevier B.V. All rights reserved.

Recently we showed that in addition to these parameters, the evaluation of the volatile point (VP) is demanded (Sanchirico et al., 2018).

To assess the explosion behavior, maximum pressure (P_{\max}), maximum rate of pressure rise ($(dP/dt)_{\max}$) and the consequent deflagration index (K_{St}) parameters must be measured.

In the literature many works are focused on the evaluation of these parameters for both traditional (Eckhoff, 2003) and non-traditional dusts (Marmo, 2010; Marmo et al., 2018; Russo et al., 2013; Salatino et al., 2012; Worsfold et al., 2012), mixture of flammable dust with inert dust (Cashdollar, 2000; International section for the Chemical Industry, 2003) and hybrid mixtures (Bartknecht, 1989; Di Benedetto et al., 2011; Garcia-Agreda et al., 2011; Li et al., 2012; Russo et al., 2012; Russo and Di Benedetto, 2013).

Conversely, not exhaustive studies have been performed yet on the behavior of mixture of flammable dusts. Furthermore, standard procedures to assess flammability and explosion parameters for pure dusts are well established (ASTM E1226-12a, 1988; ASTM E1491-06, 1991; ASTM E1515-14, 1993; ASTM E2019-03, 1999; ASTM E2019-03, 1999; ASTM E2021-15, 1999; ASTM E2021-15, 1999; ASTM E2931-13, 2013), while for mixtures of flammable dusts standard procedures have not been properly developed yet. In many cases, when dealing with mixtures of flammable dusts, as the flammable/explosion parameter is set at the value of the most dangerous. In a previous paper, we measured the VP, i.e. the minimum temperature at which volatiles given off by a dust form an ignitable mixture with air, for several mixtures of dusts (Sanchirico et al., 2018).

Surprisingly, we found that VP can be markedly influenced by the mixture composition, reaching significantly lower values than those recorded for pure dusts (VP coincides with Flash Point for pure compounds). In order to understand the reason for this behavior, we studied the thermal behavior of niacin/anthraquinone mixtures through simultaneous Thermogravimetric – Differential Scanning Calorimetric (TG/DSC) analysis (Portarapillo et al., 2020). The results revealed the presence of a eutectic point which leads to a significant reduction of the melting point and/or of the sublimation/boiling point thus accelerating the dusts ignition and then flame propagation in the gaseous phase.

In this work, we aim at investigating the flammable and explosive behavior of dust mixtures by measuring MIT, MIE, P_{\max} and K_{St} of binary mixtures, at changing relative amount of the dusts. All the mixtures were also analyzed by DSC and subsequent chemical analysis by HPLC and ATR-FTIR in order to unveil the physical and chemical transformations, as well as formation of intermediate chemical compounds underlying the flammable/explosive behavior of each dust mixture.

2. Materials and methods

2.1. Materials characterization

We characterized the behavior of glucose, niacin, L-ascorbic acid, anthraquinone, Irganox 1222 and their mixtures. Niacin (nicotinic acid, $C_6H_5NO_2$) is an organic compound classified as a B-vitamin. It is mainly used in pharmaceutical industries and it is also a reference dust for testing dust explosion. Anthraquinone (9,10-dioxoanthracene, $C_{14}H_8O_2$) is an aromatic compound. It is used in the production of dyes and natural pigments, as catalyst in the production of wood pulp and paper industry, and as laxative in pharmaceutical industry. Glucose ($C_6H_{12}O_6$) is the most abundant monosaccharide, a subcategory of carbohydrates. Glucose powder may be added to foods as a sweetening agent. L-Ascorbic acid ($C_6H_8O_6$) is a water-soluble vitamin, known as vitamin C, acting as a coenzyme, a flour treatment agent, a food antioxidant as well as a plant metabolite. Irganox 1222 (2,6-di-*tert*-butyl-4-(diethoxyphosphorylmethyl) phenol, $C_{19}H_{33}O_4P$) is a polymer additive with antioxidant properties.

All samples were purchased from Sigma-Aldrich (except Irganox 1222, provided by Kuhner AG) and characterized as received. For

characterization, scanning electron microscopy (SEM) (Philips mod. XL30) was used and the images were acquired using different magnifications. A laser diffraction granulometer (Malvern Instruments Mastersizer, 2000) was used to measure the granulometric distribution of dusts.

2.2. Characterization of flammable behavior

The approach used to conduct the experimental campaign is divided into three parts.

Flammable and explosive behaviors of pure dusts and mixtures were characterized first. Minimum ignition temperature (MIT), minimum ignition energy (MIE), maximum pressure (P_{\max}) and deflagration index (K_{St}) were determined using standard testing procedures. A thermal screening by means of differential scanning calorimetric analysis (DSC) of pure dusts and mixtures was then performed. The analyzed mixtures were 25%comp(A)/75%comp(B), 50%comp(A)/50%comp(B), 75%comp(A)/25%comp(B) by weight. Finally, in order to assess the occurrence of any chemical interaction between the dusts, HPLC and ATR-FTIR analyses were performed.

MIT of dust/air mixtures is the lowest temperature at which the dust/air mixtures will self-ignite under specified conditions. MIT of dust/air mixtures is measured in the “Godbert-Greenwald” furnace. The “Godbert-Greenwald” furnace test apparatus includes a heated quartz furnace tube with a volume of 0.27 L, two thermocouples, a sample container, an electromagnetic valve, a heater and a stop stock. The tube with bottom exposure is insulated and equipped with thermostatically controlled electric resistance wires. After setting the temperature of the furnace at the desired value, a weighed amount of dust is placed in the sample container, and then the sample is dispersed into the test chamber forming dust clouds by compressed air of 0.08 MPa after opening the electromagnetic valve. During the experiment, the flame can be observed underneath the furnace tube (ASTM E1491-06, 1991). The minimum ignition energy (MIE) was determined by means of a MIKE 3 device (Kuhner, CH), according to the ASTM E2019-03 standard (ASTM E2019-03, 1999; ASTM E2019-03, 1999). Samples (size 300–2400 mg) were dispersed through a mushroom shaped nozzle in a modified Hartman tube. Using different time delays (typically 60, 90 and 120 ms), from the air blast used for the dispersion of the dust, an electrostatic spark was triggered between the tips of a couple of tungsten rods (spark gap: 6 mm) by releasing the energy stored in a condenser bench. In all the cases, an inductance of 1 mH (prolonged sparks) was coupled to the capacitive electric circuit. The maximum pressure (P_{\max}) and deflagration index (K_{St}) were measured in the 20 L Siwek sphere, according to the ASTM E1226-12a standard (ASTM E1226-12a, 1988). The ignition source is placed at the center of the sphere through a couple of Teflon electrodes fixed to a flange located on the top of the combustion chamber. Chemical igniters of 200 J (2×100 J) were used. The chemical igniters are activated electrically by a low-voltage source and provide a dense cloud of hot dispersed particles with very little gas by-product. The delay time (60 ms) was set constant for all tests performed. 10 g sample (stoichiometric value) was placed into the dust container. The explosion chamber, which was initially filled with air at atmospheric pressure, was then evacuated to 0.6 bar absolute. An automatic test sequence was initiated to pressurize the dust container to 20 bar gauge, and then the fast-acting valve on the dust container outlet was opened to inject dust into the explosion chamber through a rebound nozzle. The rebound nozzle should ensure an uniform distribution of dust within the explosion chamber (ASTM E1226-12a, 1988). Differential scanning calorimetry thermograms were recorded with a heat power compensation DSC (PerkinElmer DSC 8000 instrument), calibrated for the enthalpies measurements and equipped with an Intracooler II apparatus. Approximately 3 mg sample was weighed into stainless-steel high-pressured pans (volume 50 μ L, Perkin Elmer Part n. B016-9321). Dry nitrogen was used as purge gas at a flow rate of 20 mL/min. Data were collected at a heating rate of 20 °C/min

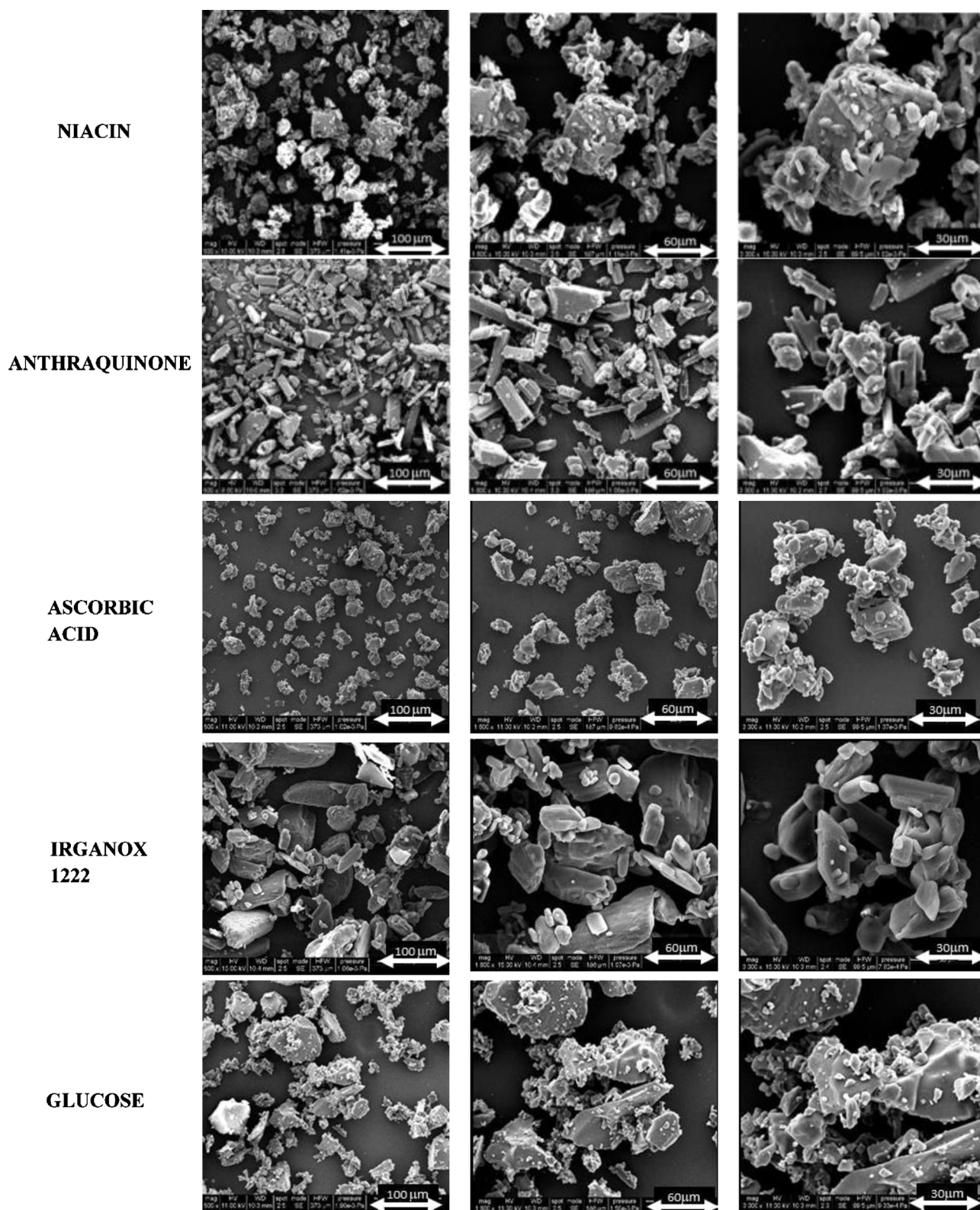
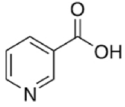
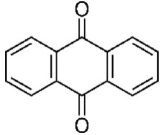
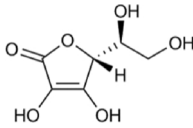
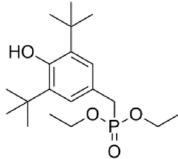
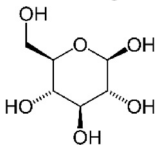


Fig. 1. SEM images of all dusts investigated at 800 \times (left), 1600 \times (center) and 3000 \times (right) magnification.

over a temperature range of 25–400 $^{\circ}$ C. The HPLC analyses were performed with an Agilent 1100 series, correlated with UV lamp and analyzer. The column, used for the separation, was a Zorbax Agilent XDB-C18, 4.6 \times 150 mm, with porous silica as base. Pure acetonitrile was used as eluent agent, and the flow rate is fixed to 1 mL/min. The samples were prepared by recovering the mixture at the end of a DSC

run (almost 3 mg of dust) into 10 mL of acetonitrile. Spectra were collected in the UV–vis light range. FTIR-ATR spectra were collected using a NICOLET 5700 spectrometer (Thermo Scientific, USA) equipped with ATR Accessory with a Zn–Se crystal. Infrared spectroscopy was performed on ascorbic acid/glucose mixtures before and after a thermal treatment to assess the chemical/physical transformations.

Table 1
Percentile diameters of dusts.

Dusts	Formula	Percentile diameters (μm)			Polydispersity σ_D
		$D(0.1)$	$D(0.5)$	$D(0.9)$	
Niacin		33.85	55.30	86.98	0.96
Anthraquinone		7.36	19.20	47.16	2.07
Ascorbic acid		6.18	19.24	47.52	2.15
Irganox 1222		10.17	34.01	69.37	1.74
Glucose		6.57	12.20	23.86	1.42

3. Results

3.1. Pure dusts

3.1.1. SEM analysis and granulometric distribution

In Fig. 1, the SEM images are shown for all the dusts investigated at different magnifications. From SEM images of niacin and anthraquinone show that the samples are composed of smooth-faced prismatic particles. SEM images of L-ascorbic acid show that particles have a quietly spherical shape and high tendency to agglomeration. SEM images of irganox 1222 show non-spherical particles that tends to a soft agglomeration. SEM images of glucose show quite spherical particles surrounded with others finest particles, maybe of rice starch.

As it is well known (Eckhoff, 2003), the granulometric distributions strongly affects the explosion behavior. Details of the percentile diameters ($D(0.1)$, $D(0.5)$ and $D(0.9)$) of dusts are given in Table 1. Polydispersity (σ_D), an important parameter to influence explosion characteristics, is defined as shown in Eq. (1) and given in Table 1.

$$\sigma_D = \frac{D(0.9) - D(0.1)}{D(0.5)} \quad (1)$$

Ascorbic acid is the most heterogeneous in particle size while niacin presents the highest homogeneity.

3.1.2. MIE, MIT, P_{max} and K_{St}

In Table 2 the values of MIE, MIT, P_{max} and K_{St} measured for each dust are shown. Niacin and anthraquinone have low values of the minimum ignition energy (1.4 mJ), almost comparable to that of some gases (i.e. the minimum ignition energy of methane is equal to 1.3 mJ). Glucose and irganox 1222 have very high values, 82 and 130 mJ, respectively. As shown in Table 1, irganox has a high particles diameter which significantly affects the surface area available for the ignition. Compared to niacin, that shows the highest particles size, irganox appears to have a greater tendency to generate agglomerates, that

Table 2MIE, MIT, P_{max} and K_{St} of pure dusts.

	MIE (mJ)	MIT ($^{\circ}\text{C}$)	K_{St} (bar m/s)	P_{max} (bar)	St class
Niacin	1.4	600	262	7.5	2
Anthraquinone	1.4	670	364	10.6	3
Ascorbic acid	14	460	74	6.2	1
Irganox 1222	130	460	212	7.2	2
Glucose	82	400	4	2.8	1

strongly affect the dispersibility in a dust cloud and consequently the minimum ignition energy. It can be seen glucose owns the lowest MIT among all the analyzed powders, with a value of 400 $^{\circ}\text{C}$. Contrarily, anthraquinone presents the highest MIT value, equal to 670 $^{\circ}\text{C}$.

3.1.3. Thermal behaviour: DSC analysis

Both the flammability and explosion parameters are strongly dependent on the physical/chemical transformations the dust undergoes to during heating. The flame propagation can be divided in three phases: dust heating up to the volatile point (VP), melting/boiling/sublimation and/or pyrolysis and volatiles combustion. In order to identify these steps, we performed DSC measurements for each dust. In Fig. 2, the DSC profiles are shown for all investigated dusts.

The curve in Fig. 2 represents the DSC trend of niacin. Two peaks are found. The former represents the niacin melting (onset temperature $\sim 233^{\circ}\text{C}$, fusion heat $\sim 200\text{ J/g}$). The latter (onset temperature $\sim 303^{\circ}\text{C}$, reaction heat $\sim -160\text{ J/g}$) can be addressed to the partial thermal decomposition of niacin.

In Fig. 2b, the DSC profile of anthraquinone is shown. One endothermic peak is found at 290 $^{\circ}\text{C}$ which is well known as the melting temperature (Domalski and Hearing, 1996). On increasing temperature, up to 400 $^{\circ}\text{C}$, the sample does not show any transformation. Devolatilization phenomena occurs at higher temperature (Portarapillo et al., 2020).

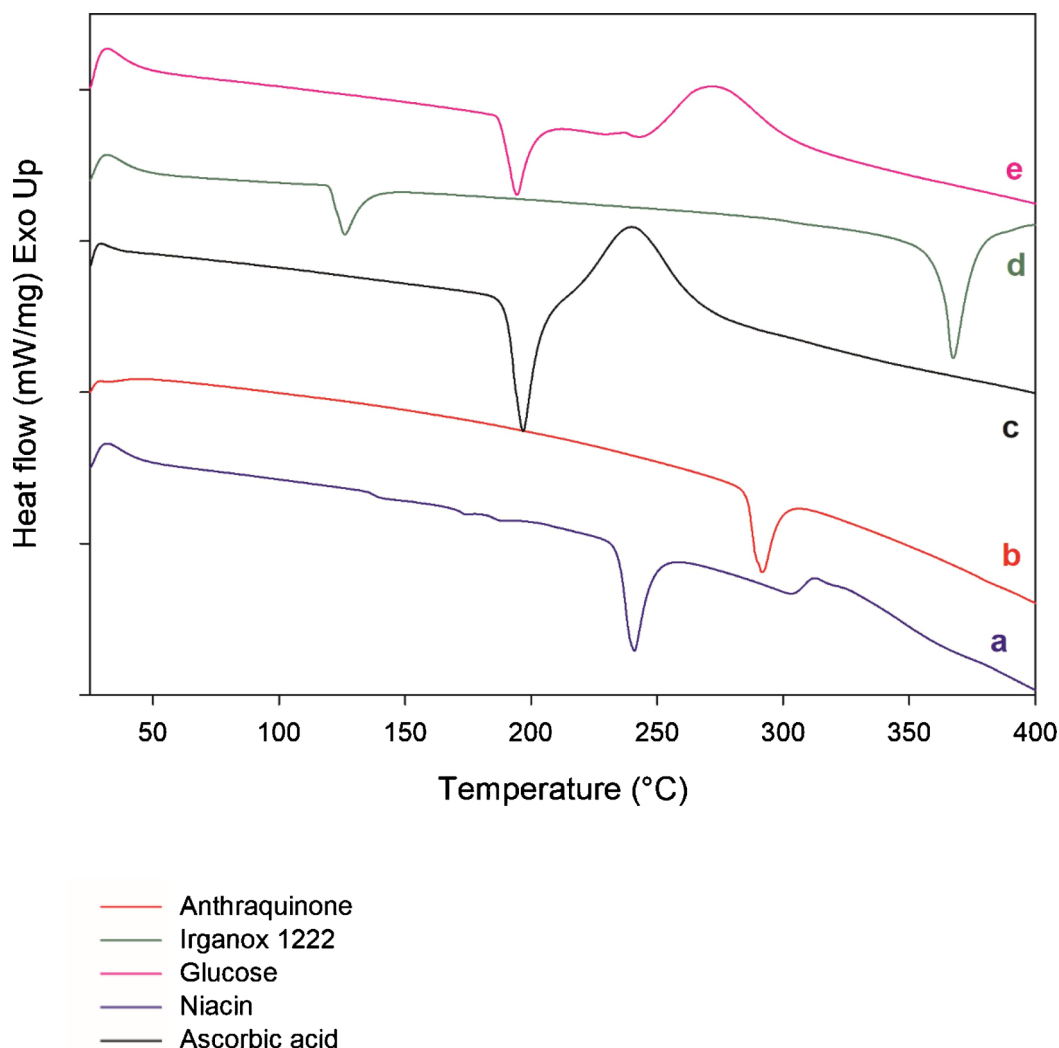


Fig. 2. DSC curves for all investigated pure dusts.

Table 3
Peak temperature and nature.

Dust	1st peak (endothermic)	2nd peak endothermic	2nd peak exothermic
Niacin	233	–	303
Anthraquinone	290	–	–
Ascorbic Acid	190	–	250
Irganox	125	368	–
Glucose	190	–	270

Fig. 2c shows the DSC curve for ascorbic acid. Two main peaks are found: one endothermic peak at 190 °C, related to the melting process, in agreement with literature data (“NIST Standard Reference Database 69: NIST Chemistry WebBook,” 2018), and an exothermic peak at higher temperature (~250 °C) related to an oxidative decomposition process, as found in the literature. The main decomposition process occurs in three stages. In the first stage, decarboxylation and dehydration are the main decomposition reactions, in the second, further decarboxylation and decarbonylation occur. At the third stage (only a slow carbonization process takes place. The decomposition of ascorbic acid produces a series of furan derivatives, in which the main product is furfural (Jingyan et al., 2013).

In Fig. 2d, the DSC result as obtained for the irganox 1222 sample is shown. In this case, two endothermic peaks are found: 125 °C and 368 °C. The first peak may be addressed to the sample melting while the

second peak is a boiling event. The predicted boiling temperature of irganox 1222 is estimated of about 417.0 ± 33.0 °C at 760 mmHg (Royal Society of Chemistry, 2020). Literature data showed that the main product of irganox 1222 decomposition is 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (Bartsch et al., 2018) at higher temperature (700 °C).

DSC curve of glucose (Fig. 2e) shows the presence of two main peaks: the former endothermic peak (190 °C) is related to melting while the latter exothermic peak (270 °C) to the occurrence of an oxidative decomposition process.

Table 3 reports the peaks temperatures for each investigated sample.

On the basis of thermal evolution behavior, driven from thermograms we can divide the dusts into two classes:

- a Class A: dusts which undergo physical transformation (melting/boiling);
- b Class B: dusts which undergo physical transformation overlapped to a thermal decomposition.

According to our results, we classified the samples analyzed as shown in Table 4.

The combustion reaction path of the dusts differs depending on the class, as shown in the following Fig. 3.

Table 4
Dust classification.

Dust	Class
Niacin	B
Anthraquinone	A
Ascorbic acid	B
Irganox	A
Glucose	B

3.2. Dust mixtures

In the following, the results of the measurements of the flammability and explosion parameters of binary dust mixtures are discussed.

For all parameters, the weight average value is also computed according to the Le Chatelier rule (i.e. Eq. (2) for MIE):

$$MIE_{mix} = \frac{1}{\left(\frac{x_A}{MIE_A} + \frac{1-x_A}{MIE_B}\right)} \quad (2)$$

where x_A is the mass fraction of component (A), MIE_A is the minimum ignition energy of component A and MIE_B is the minimum ignition energy of component B in the mixture.

Table 5 shows the list of investigated mixtures.

3.2.1. Minimum ignition energy (MIE)

The MIE values of the niacin/anthraquinone mixture are shown in Fig. 4. At all values of the mixture composition, the MIE value is constant (1.4 mJ) and equal to the values of the pure dusts. The only exception is shown by the 50% mixture, but the difference is very small (1.6 mJ). In a previous paper, we studied the thermal behavior of niacin and anthraquinone mixtures (Portarapillo et al., 2020). We found that the dusts undergo melting and subsequent production of volatiles. We also carried out FTIR analysis which confirms that volatiles production occurs through phase transition, showing that during the thermal treatment the mixtures change their compositions but not its chemical nature. In particular, during the thermal treatment, niacin abandoned the system at a temperature lower than that of pure niacin. Thus, niacin was responsible of the production of volatiles at low temperature and, obviously, MIE of mixtures is equal to that of niacin (Portarapillo et al., 2020).

In Fig. 5, the MIE values of the ascorbic acid and glucose are shown. In this case, the MIE values are between those of the pure ones and the

Table 5
Investigated mixtures.

Mixtures
Niacin/anthraquinone
Ascorbic acid/glucose
Ascorbic acid/irganox 1222
Ascorbic acid/niacin

trend is well predicted by the Le Chatelier equation.

In the case of the ascorbic acid/irganox 1222 mixtures (Fig. 6), a different behavior is observed. In particular, the MIE values are always higher (and consequently safer) than those predicted by the Le Chatelier equation. A complex non-linear behavior is observed. The strong deviation from the Le Chatelier curve could be addressed to the different chemical structure of the pure dusts. For this reason, the energy supplied to the system is not sufficient to trigger ascorbic acid because it is largely absorbed by the heavier irganox. Given the same amount of sample, a greater energy amount than previously analyzed mixture (ascorbic acid–glucose) must be absorbed by ascorbic acid–irganox mixture to make the same temperature jump. Therefore, the higher the irganox fraction, the higher the energy supplied to get ignition.

In the case of the ascorbic acid/niacin mixtures (Fig. 7), the MIE values are always higher (and consequently safer) than those predicted by the Le Chatelier equation. The addition of even a small amount of ascorbic acid increases the MIE value (about 7 mJ) compared to that of pure niacin (1.4 mJ) while 25 % of niacin does not affect ascorbic acid MIE value. This suggests that ascorbic acid is the substance among these pure dusts that controls MIE trend.

3.2.2. Minimum ignition temperature (MIT)

In Fig. 8, the MIT values of the niacin/anthraquinone mixture are plotted. It is found that at all concentrations, the MIT values are dominated by the niacin MIT values. This result suggests that in the presence of niacin, the auto-ignition of the mixture is controlled by niacin reaction. Actually, at all investigated concentrations, the MIT value of the mixture is higher or equal to that of pure niacin. It is also worth noting that the MIT values are always lower (and more dangerous) than the value predicted by the Le Chatelier Rule.

In the case of the glucose/ascorbic acid mixture (Fig. 9), the MIT values are higher than the values predicted by the Le Chatelier equation. In this case, mixtures show a safer behavior than that expected

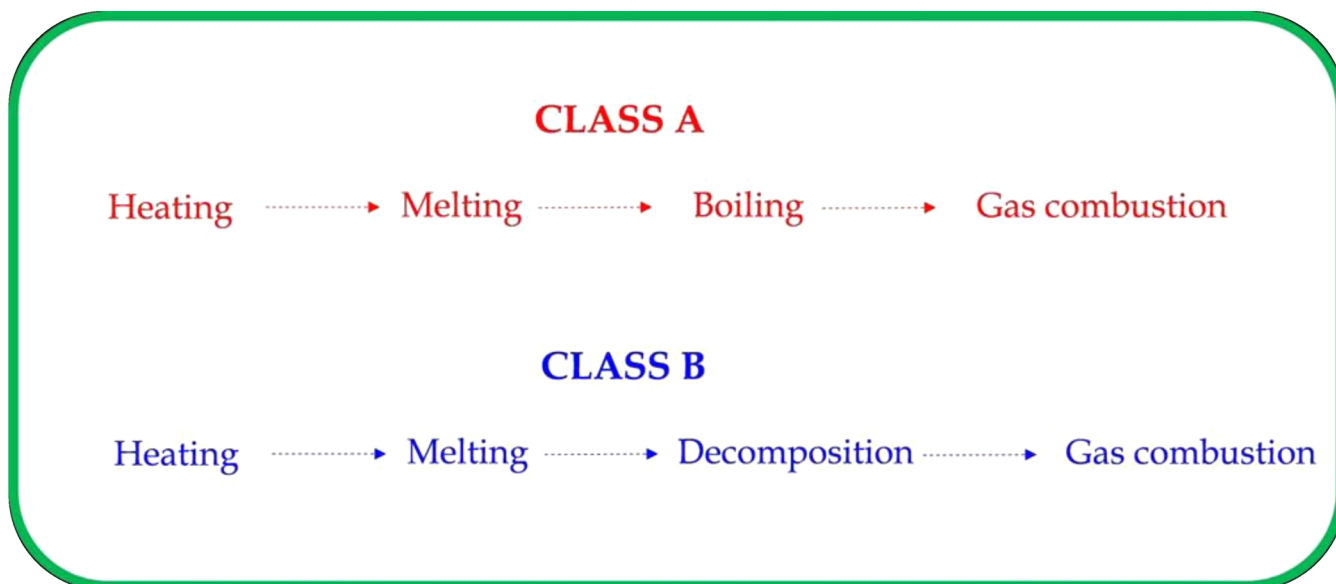


Fig. 3. Reaction path of dusts.

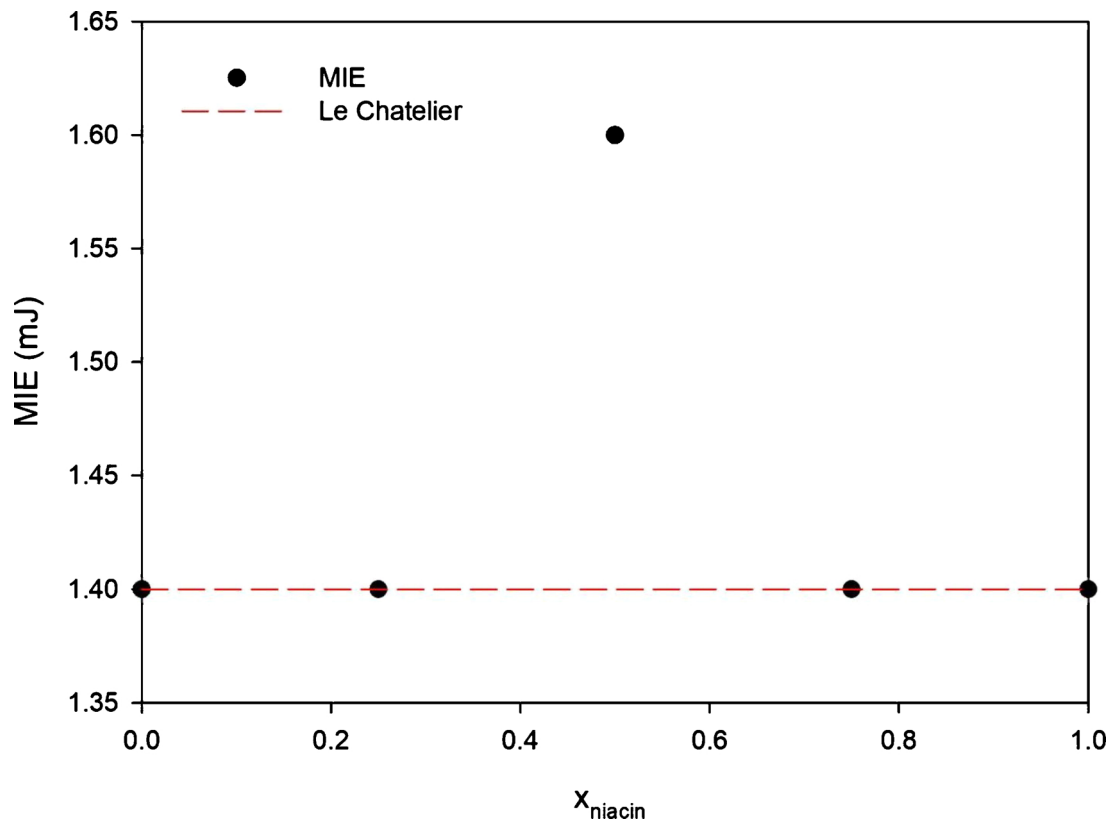


Fig. 4. MIE of niacin-anthraquinone mixtures.

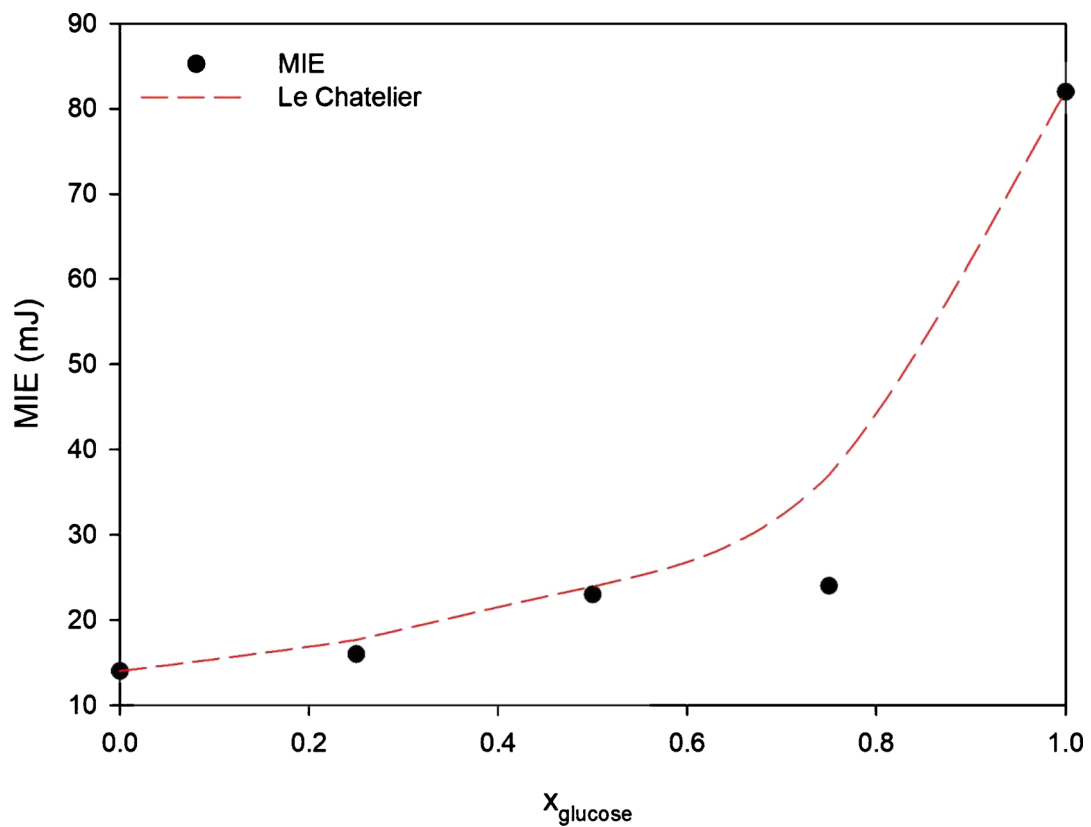


Fig. 5. MIE, ascorbic acid-glucose mixtures.

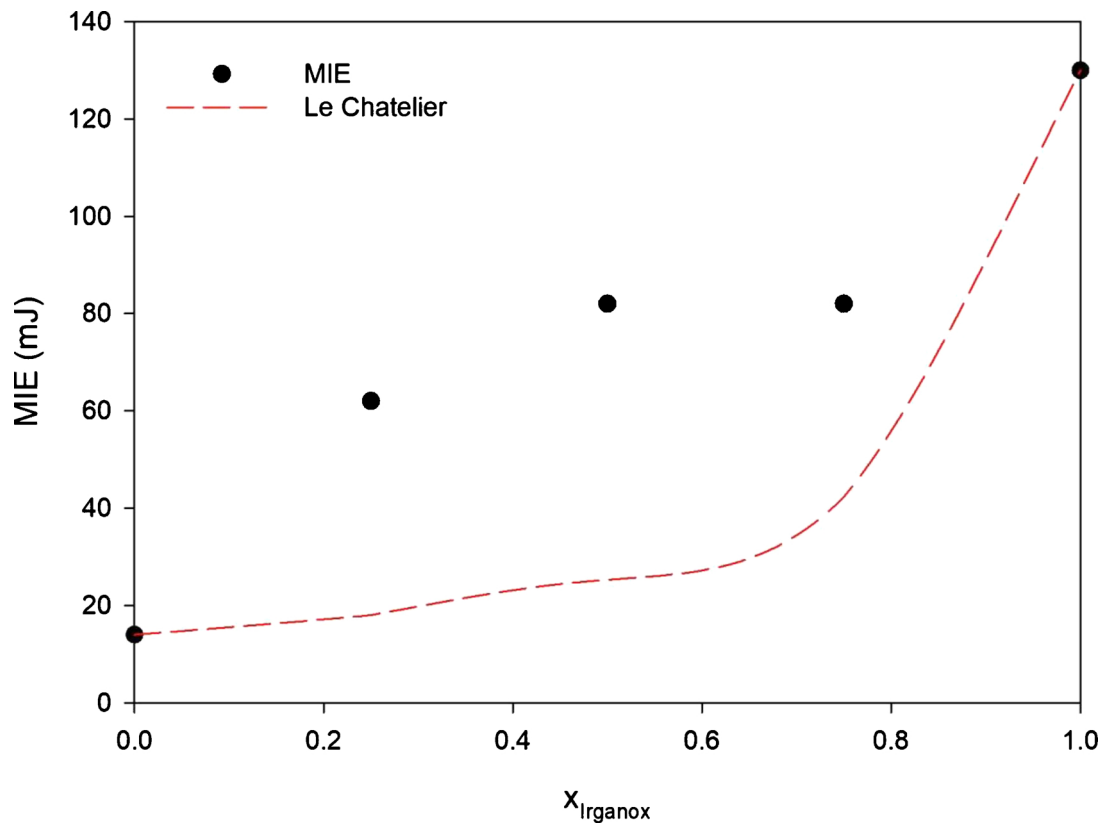


Fig. 6. MIE, ascorbic acid-irganox 1222 mixtures.

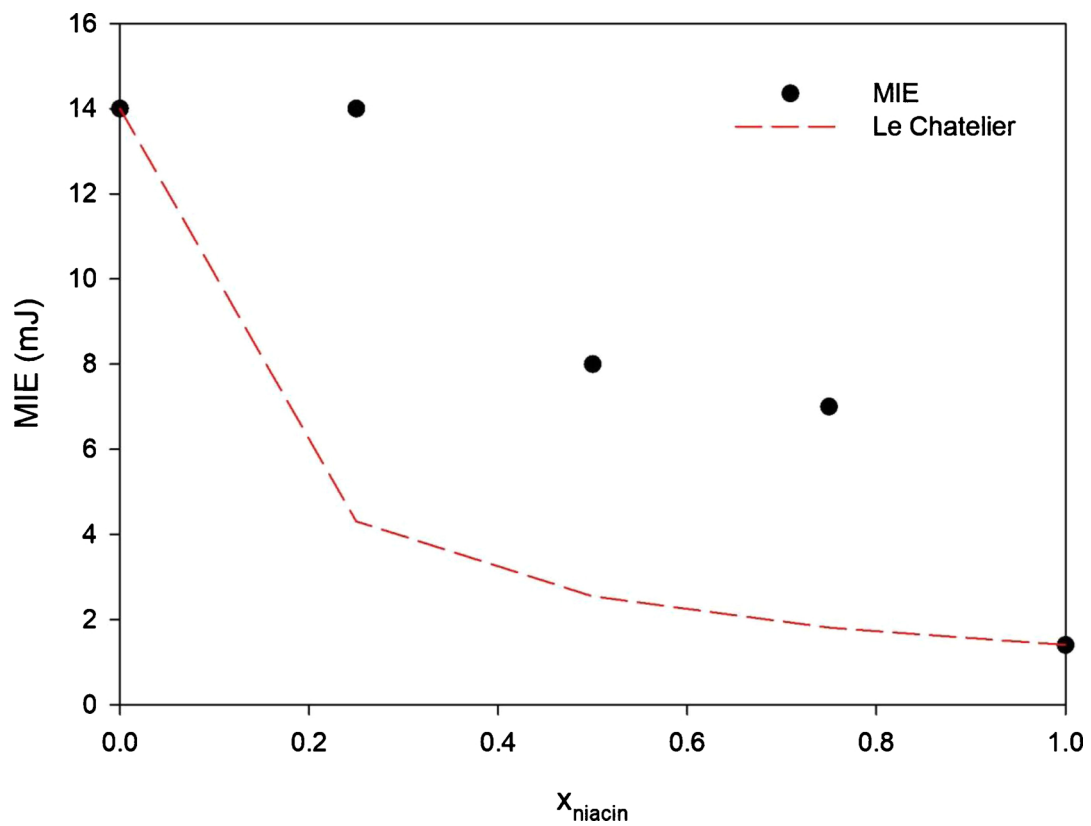


Fig. 7. MIE, ascorbic acid-niacin mixtures.

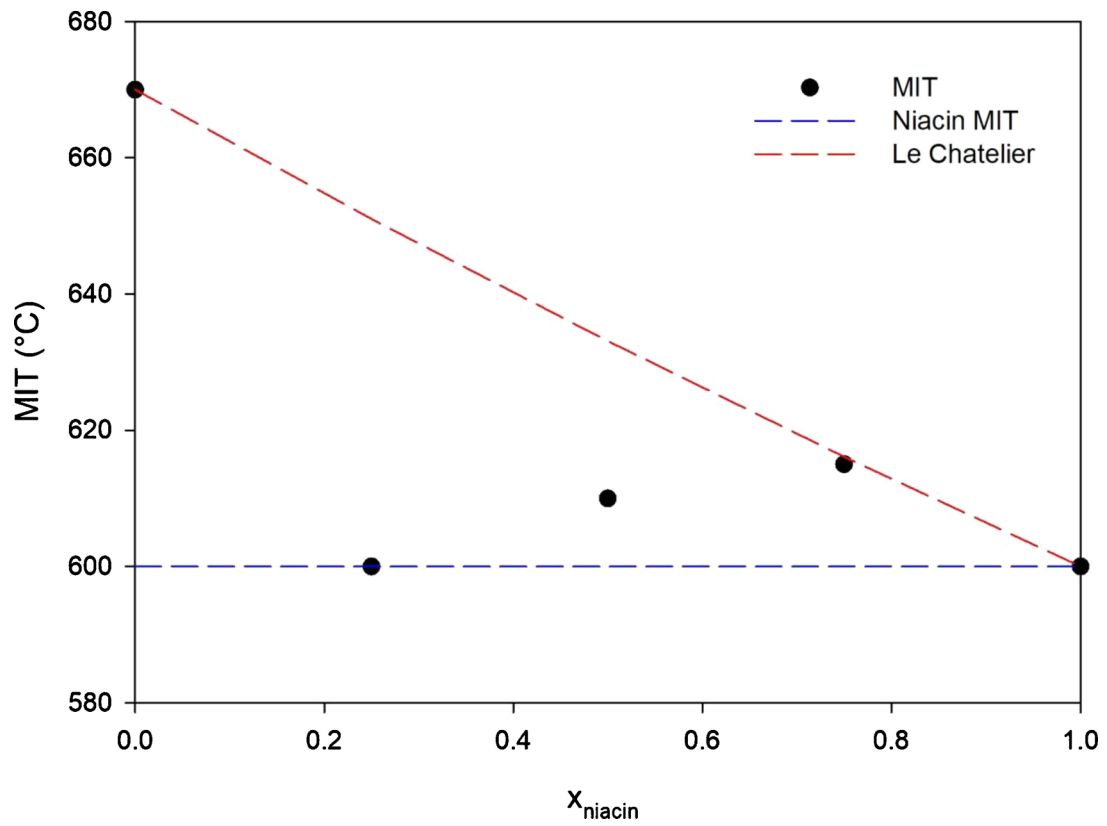


Fig. 8. MIT of niacin-anthraquinone mixtures.

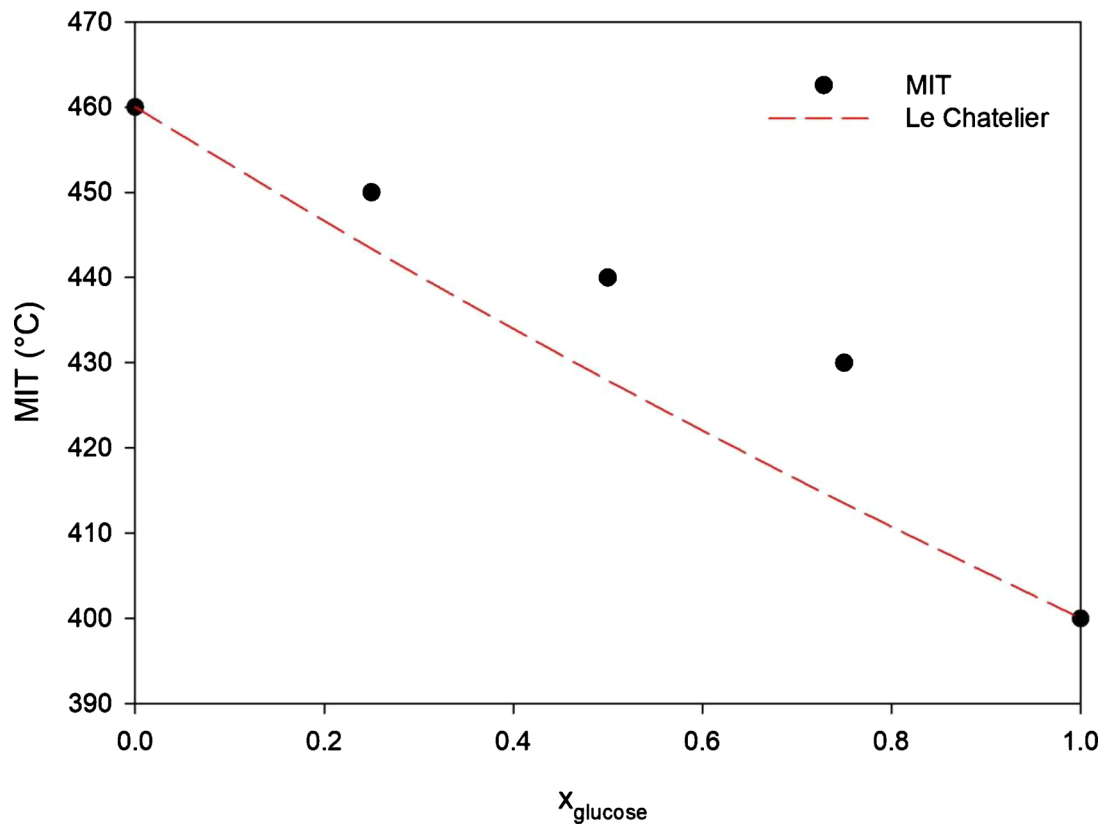


Fig. 9. MIT of ascorbic acid-glucose mixtures.

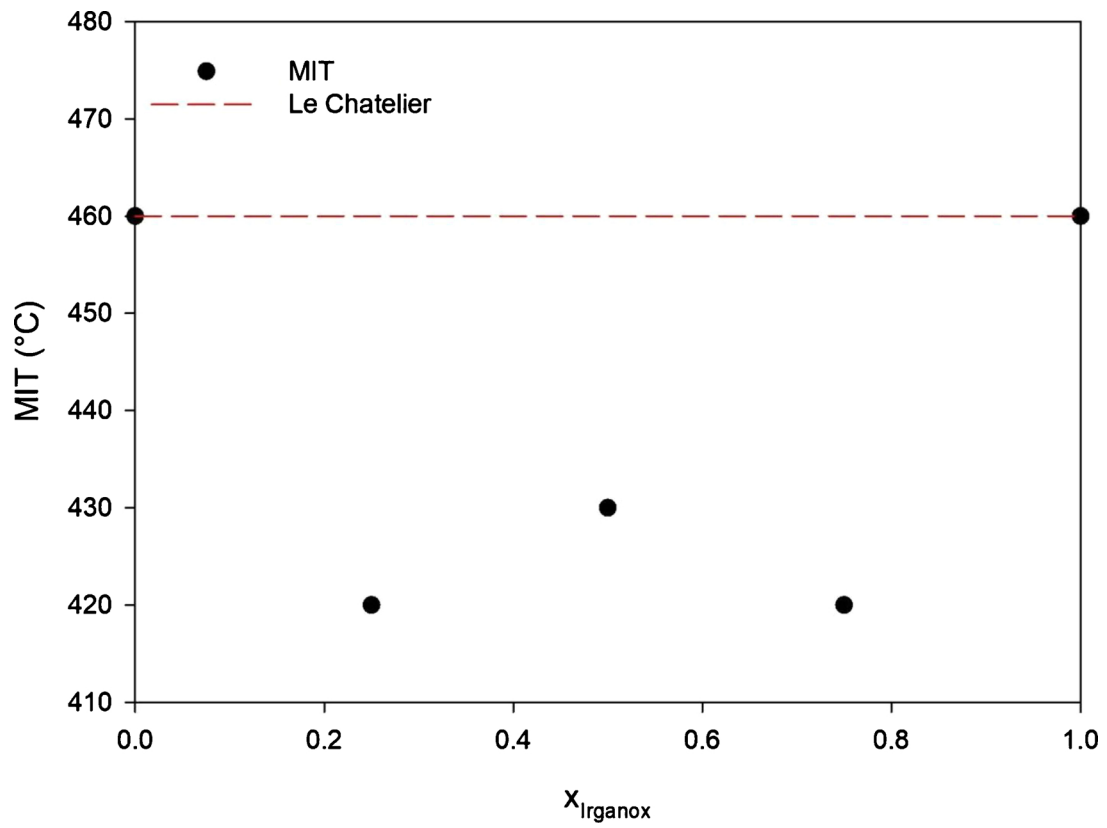


Fig. 10. MIT of ascorbic acid-irganox 1222 mixtures.

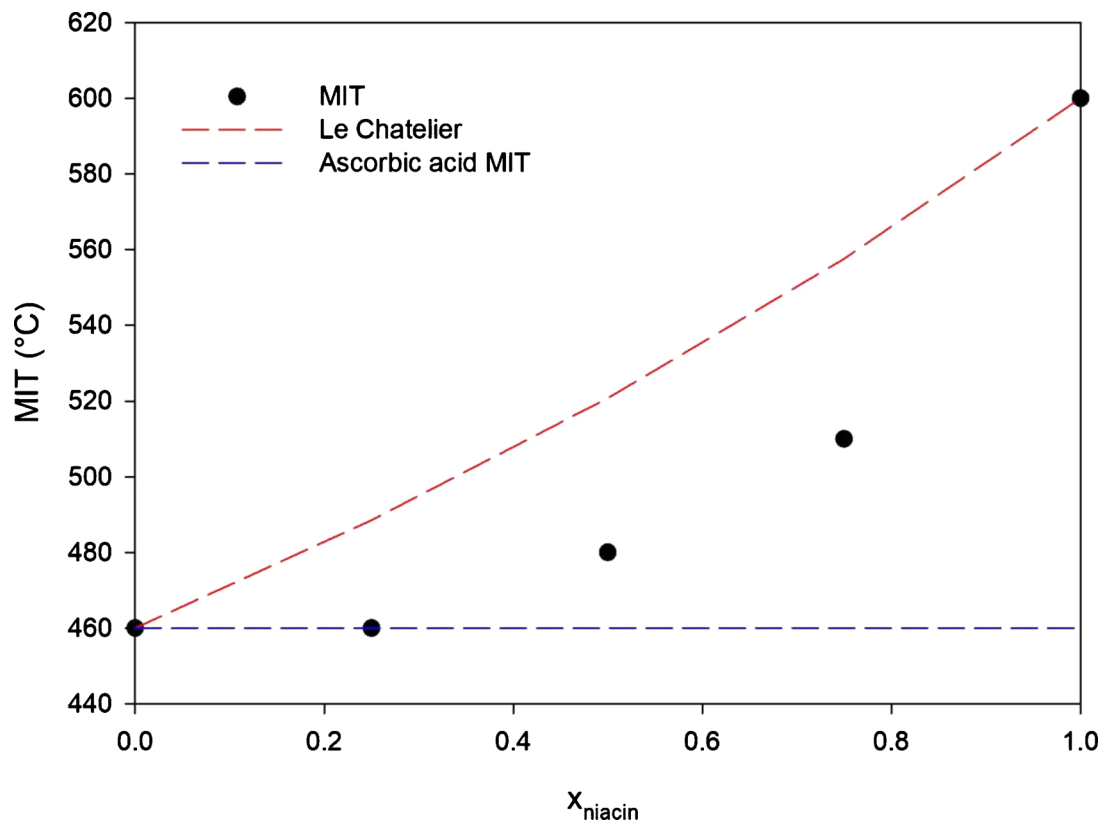


Fig. 11. MIT of ascorbic acid-niacin mixtures.

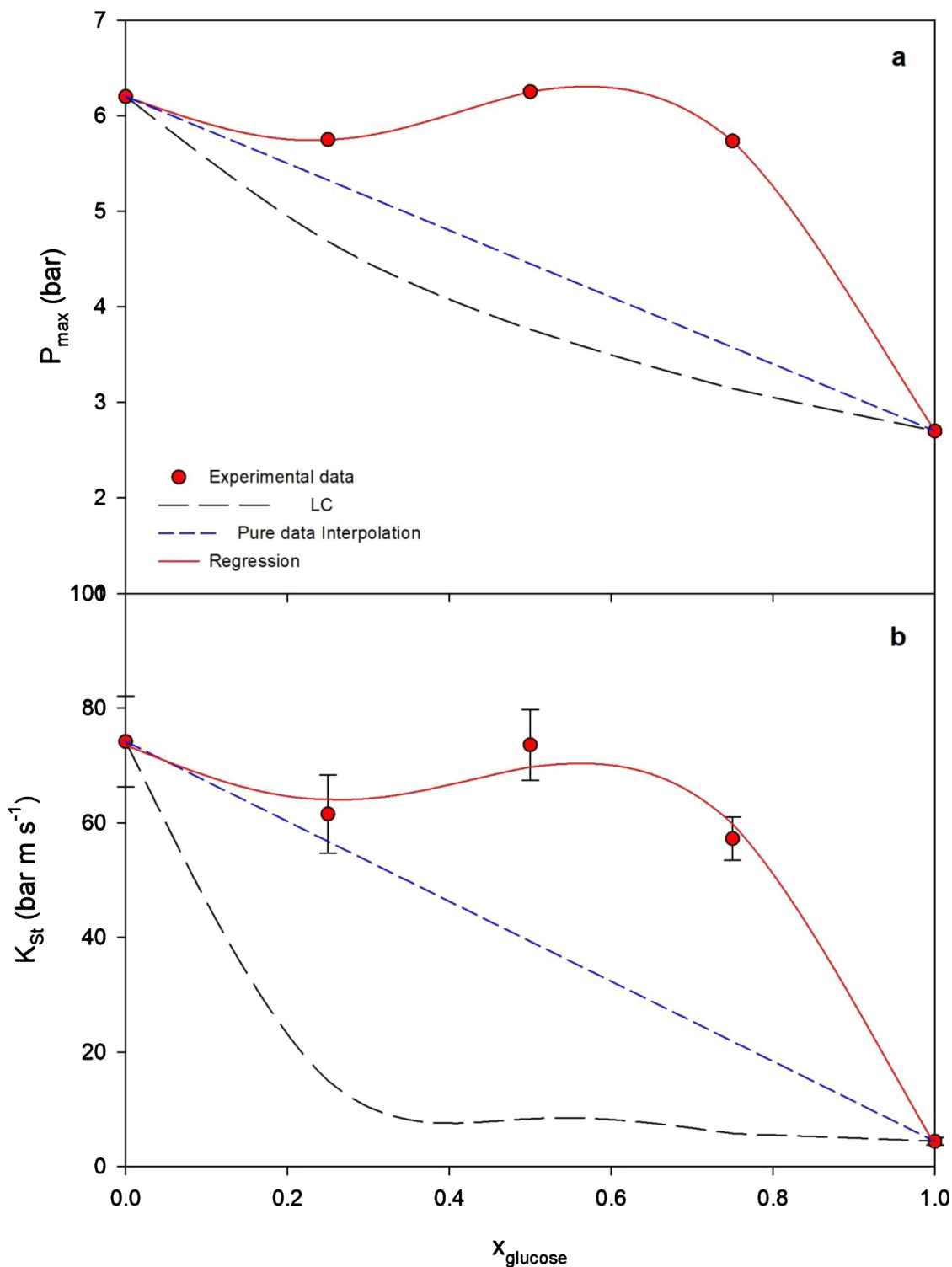


Fig. 12. P_{\max} (a) and K_{St} (b) as function of mixture composition. $C_{dust} = 500 \text{ g/m}^3$, ascorbic acid–glucose.

from the Le Chatelier curve.

In Fig. 10, the MIT values are plotted as measured for ascorbic acid–irganox 1222 mixtures. MIT of the pure samples are the same and they are equal to $460 \text{ }^\circ\text{C}$. Surprisingly, the MIT values of the mixtures are lower than $460 \text{ }^\circ\text{C}$, at all the concentrations investigated. This result suggests that a chemical and/or physical interaction between the two samples is established, generating a more severe behavior. Therefore, if safe measures are designed by taking into account the MIT values of the pure sample and ascorbic acid and irganox 1222 come into contact, the

probability of generating random explosion is extremely high due to a higher temperature than the safe upper limit for the hot surfaces.

In Fig. 11, the MIT values of the niacin/ascorbic acid mixtures are plotted. It is also worth noting that the MIT values are always lower (and more dangerous) than the value predicted by the Le Chatelier Rule. Actually, at all investigated concentrations, the MIT value of the mixtures is higher or equal to that of pure ascorbic acid.

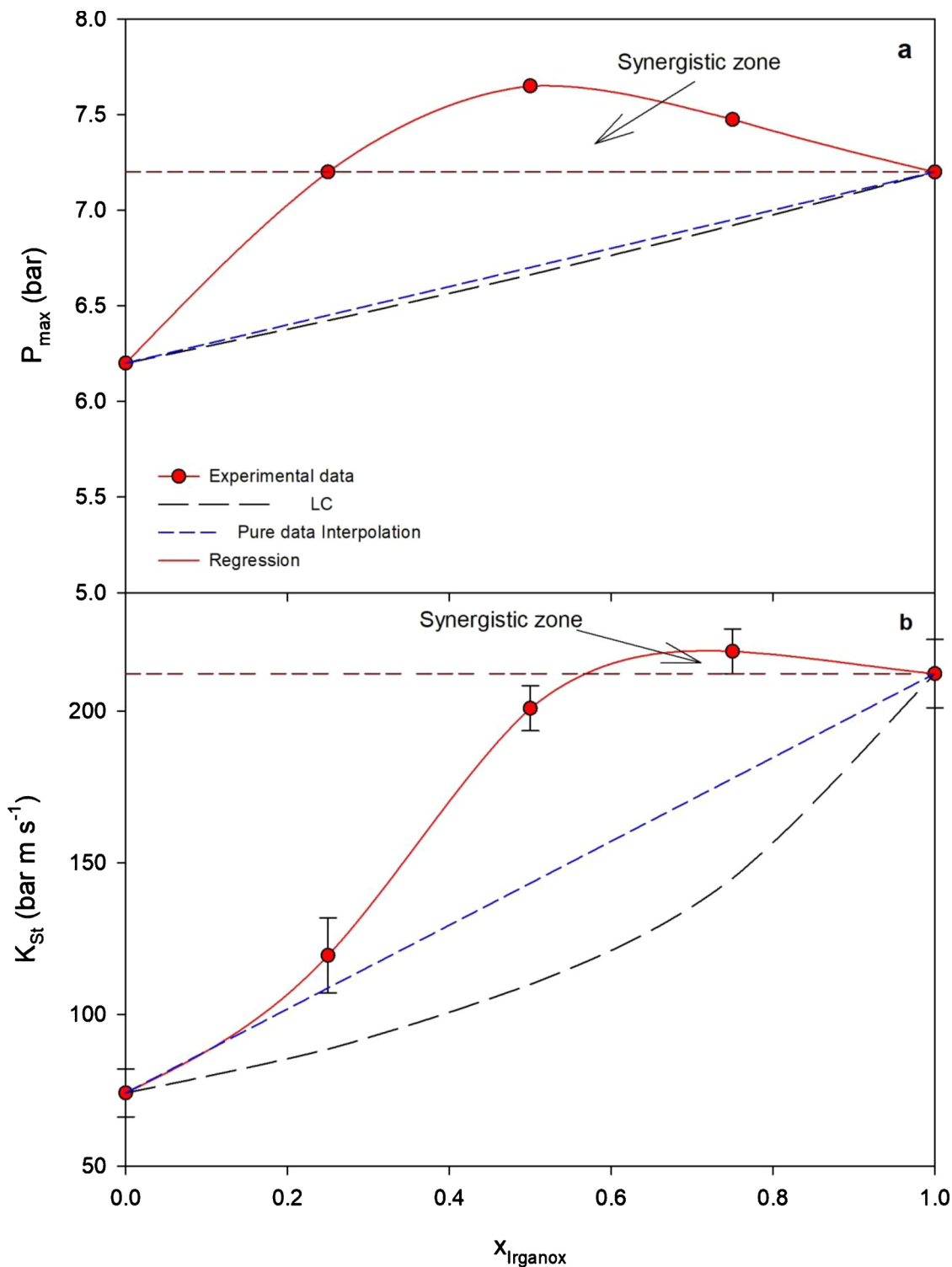


Fig. 13. P_{max} (a) and K_{St} (b) as function of mixture composition. $C_{\text{dust}} = 500 \text{ g/m}^3$, ascorbic acid–irganox.

3.2.3. Explosion parameters

Explosion tests were performed to evaluate the maximum pressure (P_{max}) and the deflagration index (K_{St}). All the tests were performed at fixed dust concentration (500 g/m^3) with two 100 J igniters.

The evaluation of these parameters in the Siwek sphere for niacin/anthraquinone mixtures have not been carried out due to the difficulties encountered in cleaning the sphere following a test involving anthraquinone. In Fig. 12, the P_{max} (a) and K_{St} (b) are plotted versus the glucose amount in the ascorbic acid–glucose mixtures.

At all dust mixtures compositions (x_{glucose}), the deflagration index is lower than the values of the K_{St} of the pure ascorbic acid dust, except at $x_{\text{glucose}} = 0.5$ where the deflagration index is equal to the value of pure ascorbic acid. It is worth noting that the explosion phenomenon is controlled by ascorbic acid explosion since the K_{St} values are very similar to that of pure ascorbic acid, even at high glucose concentration ($x_{\text{glucose}} = 0.8$). In all cases, the K_{St} is always higher than the values predicted by Le Chatelier equation (LC).

In Fig. 13, the explosion parameters are shown as obtained for the

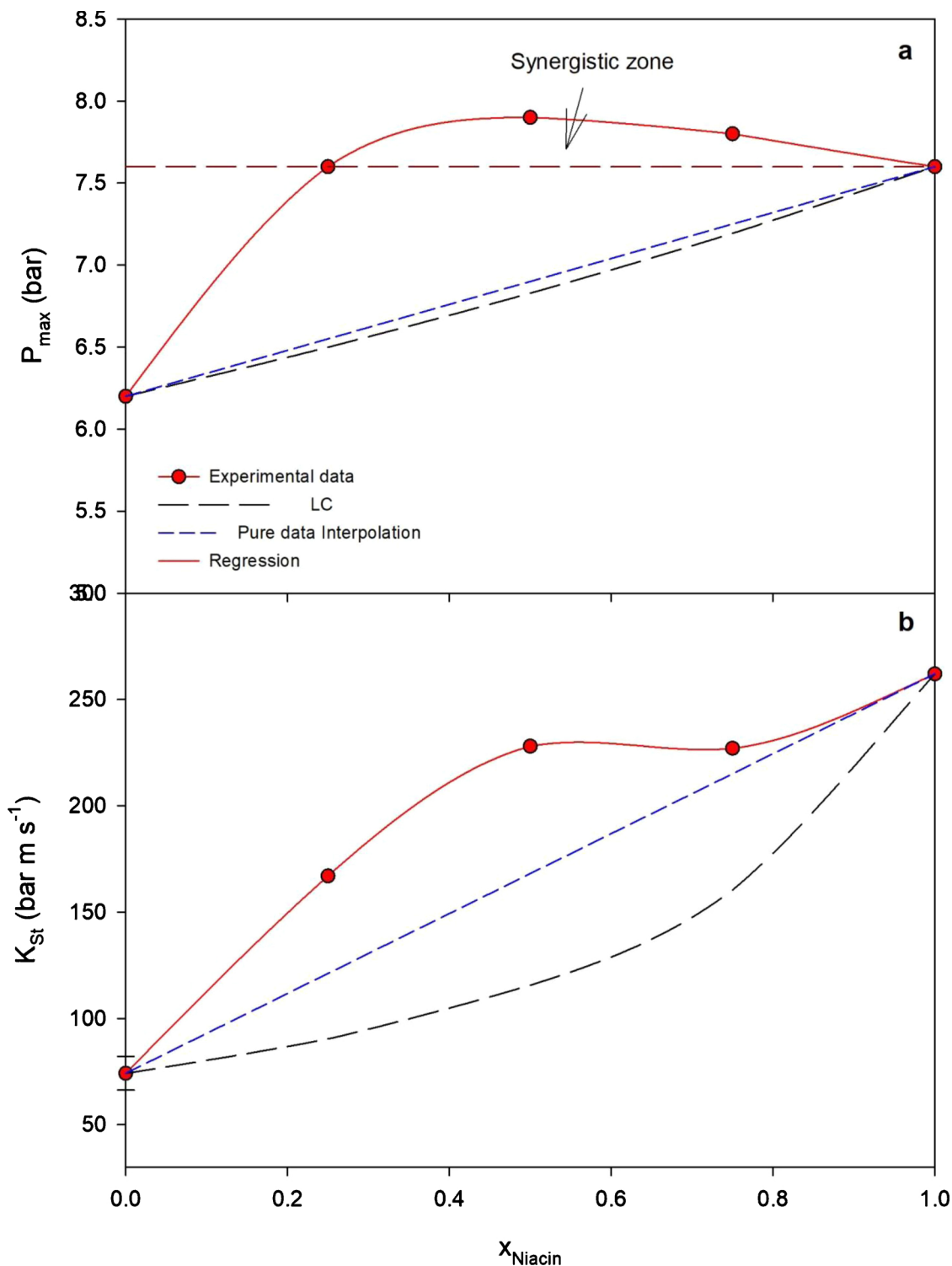


Fig. 14. P_{max} (a) and K_{St} (b) as function of mixture composition. $C_{\text{dust}} = 500 \text{ g/m}^3$, ascorbic acid–niacin.

mixtures irganox–ascorbic acid at total dust concentration equal to 500 g/m^3 . On increasing the irganox concentration, both maximum pressure and deflagration index overcome the pure values, suggesting that some physical and/or chemical reactions are playing a role.

In the case of the niacin/ascorbic acid mixture, a significant increase of the explosion parameters compared to the pure dusts values is found (Fig. 14).

3.2.4. Thermal behavior of dust mixtures: DSC analysis

In the following the DSC analysis results are discussed as obtained for niacin/antraquinone, ascorbic acid/glucose, ascorbic acid/irganox 1222 and niacin/ascorbic acid mixtures. In a previous paper we already performed TG/DSC analysis of niacin and anthraquinone mixtures (Portarapillo et al., 2020). We found that the dusts undergo melting and subsequent production of volatiles. We also carried out FTIR analysis which confirms that volatiles production occurs through phase transition, showing that during the thermal treatment the mixtures change

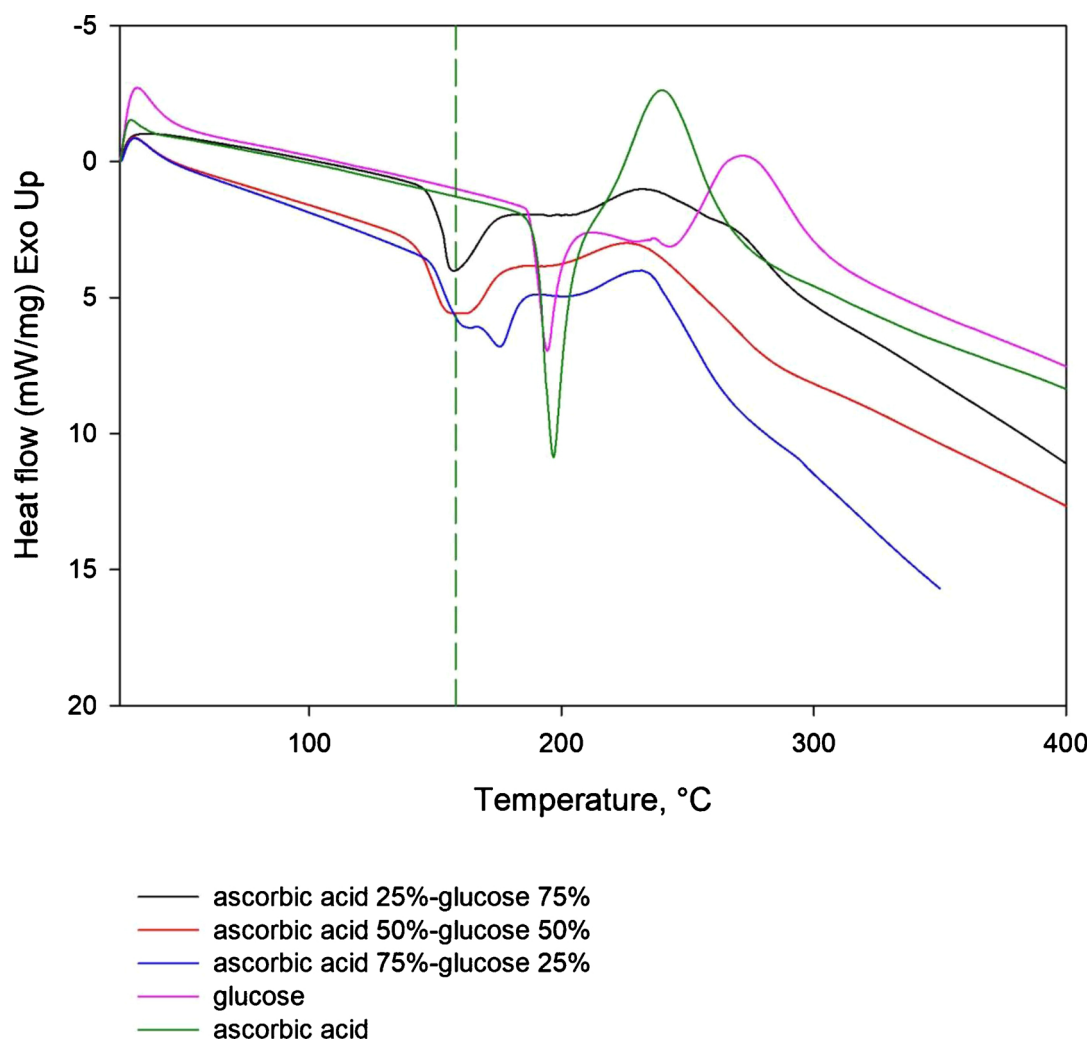


Fig. 15. DSC curves, ascorbic acid/glucose, all mixtures.

their compositions but not its chemical nature. This analysis revealed the presence of a eutectic point which leads to a significant reduction of the melting point and/or of the sublimation/boiling point. This behavior was addressed as the phenomenon controlling the decrease of the volatile point (VP) of the mixture with respect to the pure dusts. Therefore, volatiles production is observed at lower temperature than pure dusts, as for volatile ignition/combustion (Portarapillo et al., 2020). This phenomenon has the flammability parameters markedly deviated from the Le Chatelier curve (Fig. 8).

Fig. 15 shows the DSC curves obtained for ascorbic acid/glucose mixtures, at changing the mixture composition. Ascorbic acid and glucose have the same melting temperature. Two main zones are found: the former is related to endothermic phenomena, while the latter to an exothermic process. In the endothermic zone, three peaks are superimposed in the same low temperature range: the first peak is always found at about 155 °C, which is lower than the fusion temperature of pure dusts (190 °C). It is reasonable to assume that even in this mixture a eutectic point may be present at about 155 °C for a mixture containing 25% of ascorbic acid, thus a physical interaction between pure dusts occurs. After the endothermic zone, whatever the content of glucose, a marked decrease is observed for oxidative decomposition peaks, suggesting a decrease of its amount in the condensed phase. Therefore, the occurrence of a eutectic point and an endothermic reaction in the same temperature range has to be taken into account. Actually, the formation of furan (volatiles) from sugars, ascorbic acid, and organic acids as affected by thermal treatments was deeply investigated (Fan, 2005;

Limacher et al., 2007). To assess the presence of a chemical reaction within the endothermic zone, a sample of ascorbic/glucose mixture at 50% of glucose was treated up to 190 °C (end of endothermic zone) and rapidly quenched. The solid residue was tested through infrared analysis (ATR-FTIR) (Fig. 16). After thermal treatment, the spectrum is different from the initial one. The spectrum of the treated mixture appears more smoothed and intense than the pure mixture. Notably, bands in the range 3000–3500 cm^{-1} and 1000–1500 cm^{-1} grow more intense and smoother, as typical of oligosaccharide moieties. These features suggest glucose polymerization occurred during thermal treatment (Wiercigroch et al., 2017). As a further support, recovered solid residue appeared in molten form, amber in color with a consistency similar to caramel. The IR spectra and the aspect of the treated sample show the occurrence of a chemical process within the endothermic zone. Thus, the deviation from the theoretical behavior is caused by physical and, more deeply, by chemical reaction within the endothermic zone.

In Fig. 17 the DSC curves obtained for the ascorbic acid and niacin mixture are shown, at changing the mixture composition. With only 25% of vitamin C, the DSC profile is completely mutated when compared to that of pure niacin. It can be seen the appearance of three different endothermic peaks that are at temperatures slightly lower than that of ascorbic acid endothermic peak. The first endothermic peak can be associated to the occurrence of a eutectic. Immediately after the third endothermic peak, an exothermic one appears, anticipating the exothermic phenomenon of pure vitamin C. In this exothermic zone,

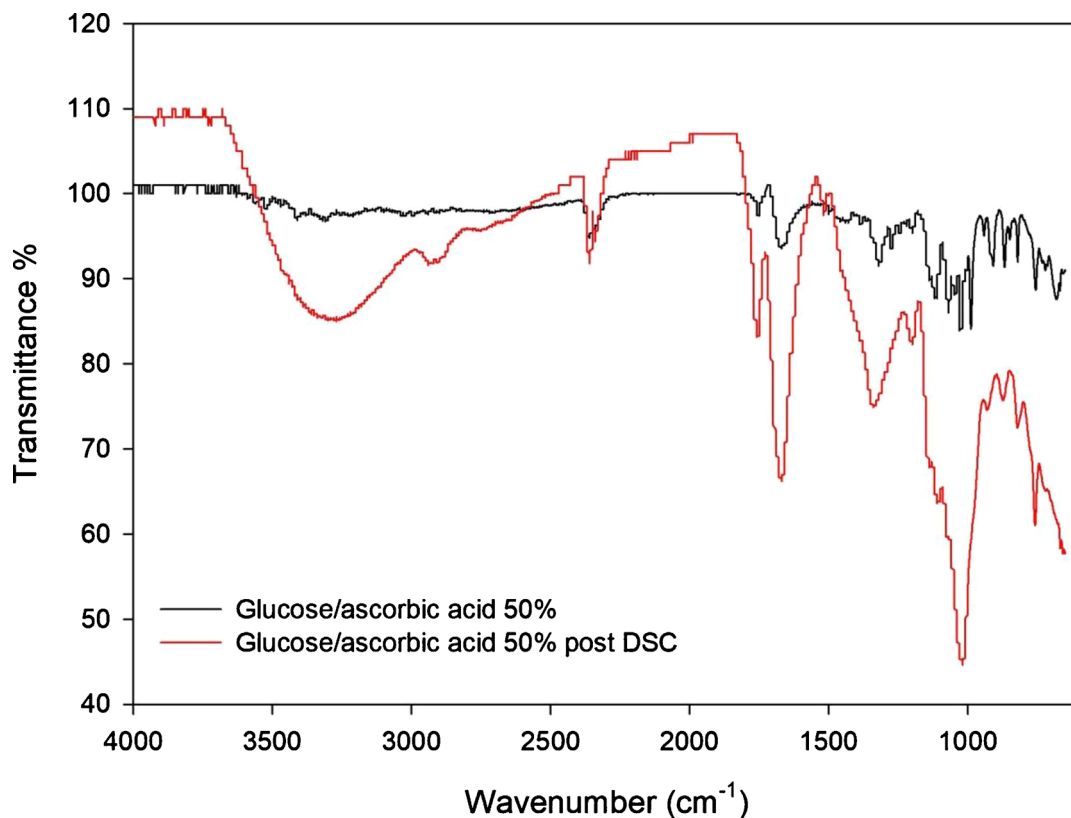


Fig. 16. ATR spectra of 50% glucose/ascorbic acid mixture before and after the thermal treatment.

pure dusts react: increasing ascorbic acid concentration, the second peak of niacin disappears due to its total consumption. By increasing the content of ascorbic acid, the peak intensities increase, and the

exothermic peaks are incorporated in a single peak. To assess the occurrence of chemical reaction within the endothermic zone of DSC curve, a sample containing the 50% of niacin was treated up to 190 °C

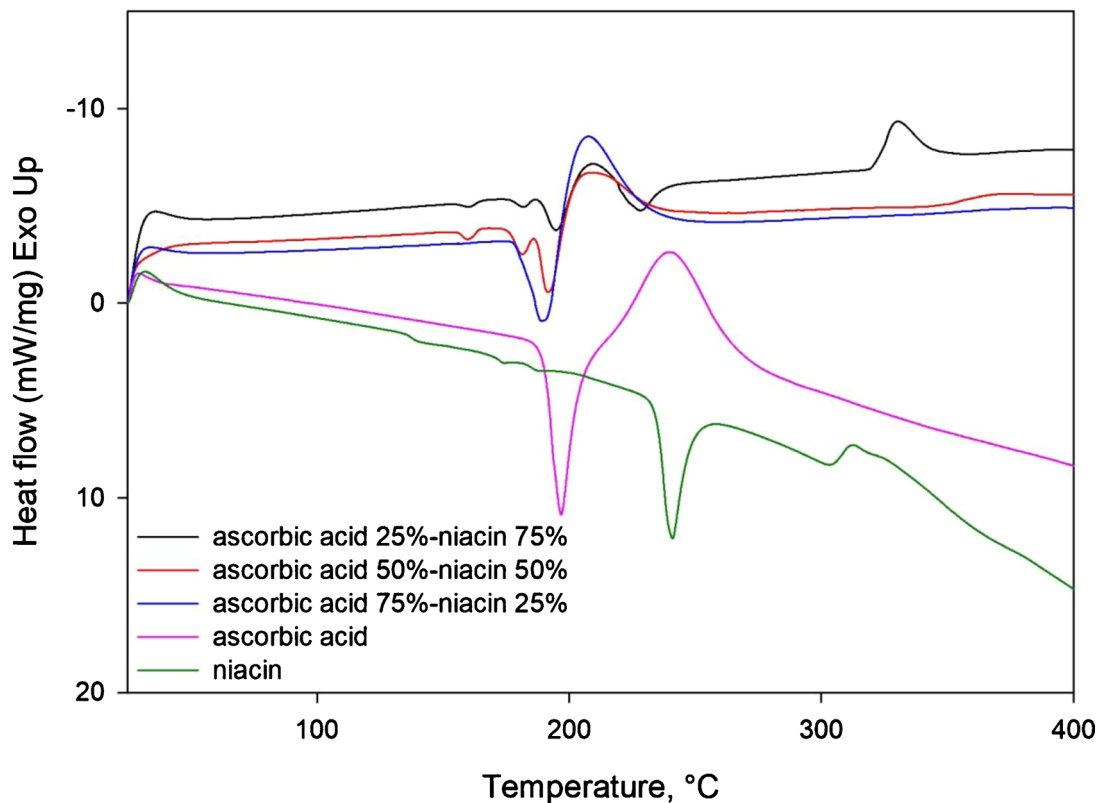


Fig. 17. DSC curves, ascorbic acid/niacin, all mixtures.

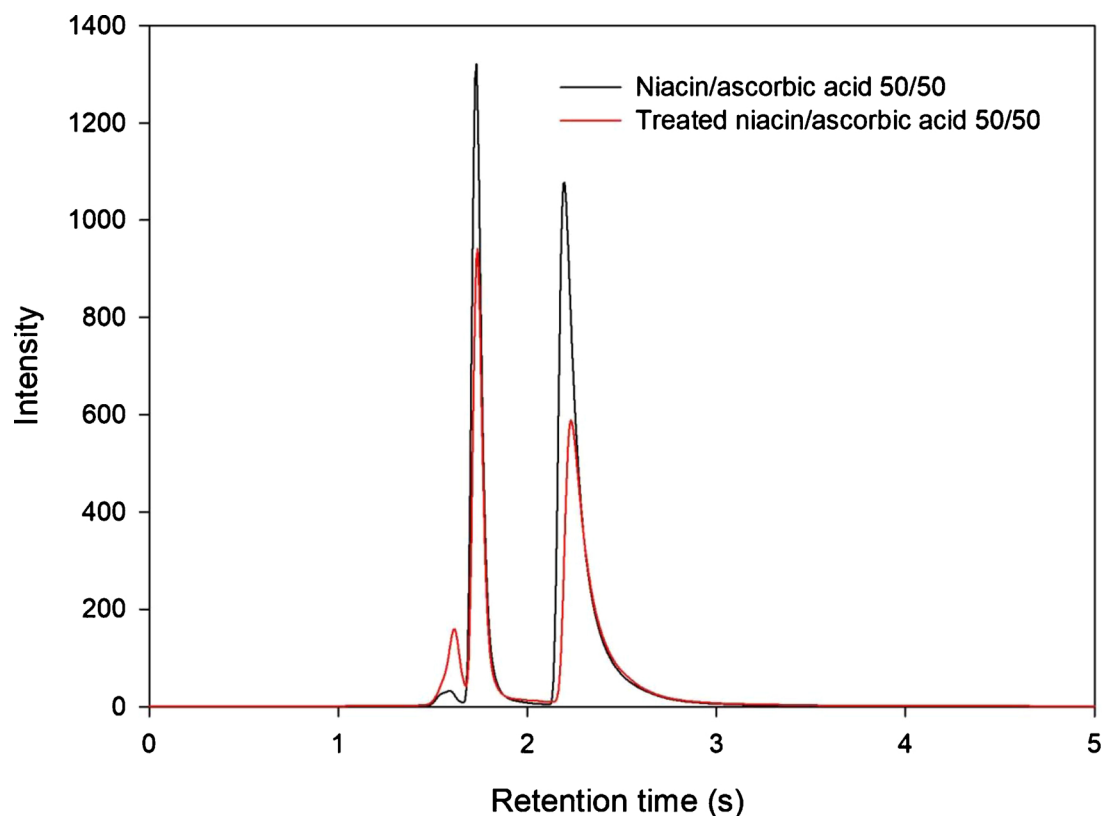


Fig. 18. Retention times profile for 50% niacin/ascorbic acid mixture, before and after the thermal treatment.

and then rapidly quenched. The solid residue was then analyzed through HPLC analysis. The characteristic retention times are respectively 1.70 min (ascorbic acid), 2.20 min (niacin) and 1.53 min (ascorbic acid impurity). Comparing the HPLC spectra, no difference can be seen between the mixture before and after the thermal treatment. Thus, no chemical reaction occurs within the endothermic zone (Fig. 18). Surprisingly, by analyzing a sample treated up to 190 °C and kept at this temperature for 5 min, a change can be observed (Fig. 19). In this new spectra, ascorbic acid characteristic peak disappears (1.70 min), leaving the niacin peak unchanged. The liquid solution, created by the fusion of niacin and ascorbic acid, favored the decomposition of ascorbic acid into volatiles at lower temperature than ascorbic acid alone.

Fig. 20 shows the DSC curves of ascorbic acid/irganox mixtures. Four phenomena may be highlighted: three endothermic ones and one exothermic peak. The first endothermic peak, related to irganox melting, has a soft anticipation. In each of the three intermediate analyzed mixtures, the temperature is lower than that of irganox of about 6–7 °C for freezing-point depression. On the contrary, the second endothermic peak, caused by the ascorbic acid melting, does not show any incisive change in peak temperature. Instead, considering the exothermic peak, related to ascorbic acid decomposition, it is possible to notice how, as the irganox concentration increases, the peaks positions tend to shift to higher temperatures and the peak intensity decreases. This peak appears to be associated principally to the content of irganox, modifying the characteristic temperature of the following endothermic peak. This peak tends more and more to anticipate towards lower temperatures by decreasing irganox 1222 content. The difference between the temperature of the irganox boiling peak and the last endothermic peak of mixtures is of about 70 °C. This anticipation could be caused by a process that occurs within the exothermic peak. This probably corresponds to ascorbic acid decomposition. Furthermore, the shape change of exothermic peak, suggests that irganox 1222 also undergoes to chemical transformation, generating products with different

boiling temperature. Actually, the formation of polymorphs of antioxidants, such as irganox 1076, when subjected to thermal treatments, has been studied (Saunier et al., 2017). In order to assess the occurrence of chemical processes, HPLC analyses were performed on ascorbic acid-irganox 1222 samples. First of all, the mixture containing 50% irganox before the thermal treatment was analyzed (Fig. 21). The characteristic retention times are respectively 1.70 min (ascorbic acid), 2.23 min (irganox) and 1.53 min (ascorbic acid impurities). Then the dust samples were first subjected to thermal treatment with DSC, heated up to the exothermic peak temperature and then rapidly quenched to room temperature with a rate of 50 °C/min. The obtained product was dissolved in acetonitrile (ACN) and analyzed with HPLC using 100% ACN flow as eluent. Fig. 22 shows the retention time profile for a mixture containing 25% of irganox and the mixture before the thermal treatment as reference. The retention time of the individuated substances are respectively: 1.531 min, 1.767 min, 2.229 min, 2.364 min, 3.164 min, 3.692 min. Different peaks appear compared to the reference, suggesting the occurrence of a chemical process with formation of new moieties. The signals of the mixtures at 50% and 75% of irganox have different intensities and retention times compared to the precedent profiles, suggesting the presence of different species (not reported). Unfortunately, it was not possible to determine the nature of the detected substances due to lack of reference spectra. Hypothesizing a probable chemical reaction mechanism between the two constituents is very difficult. Similarities among the detected spectra and those of Irgafos 168 (Agilent Technologies Inc., 2003) and butylated hydroxyanisole (Akkbik et al., 2011) were found. Both substances are antioxidants and could be produced through decomposition of Irganox 1222, protonation of the ascorbic acid and subsequent condensation of the decomposition products.

4. Discussion

Different behaviors were found for each mixture and safety

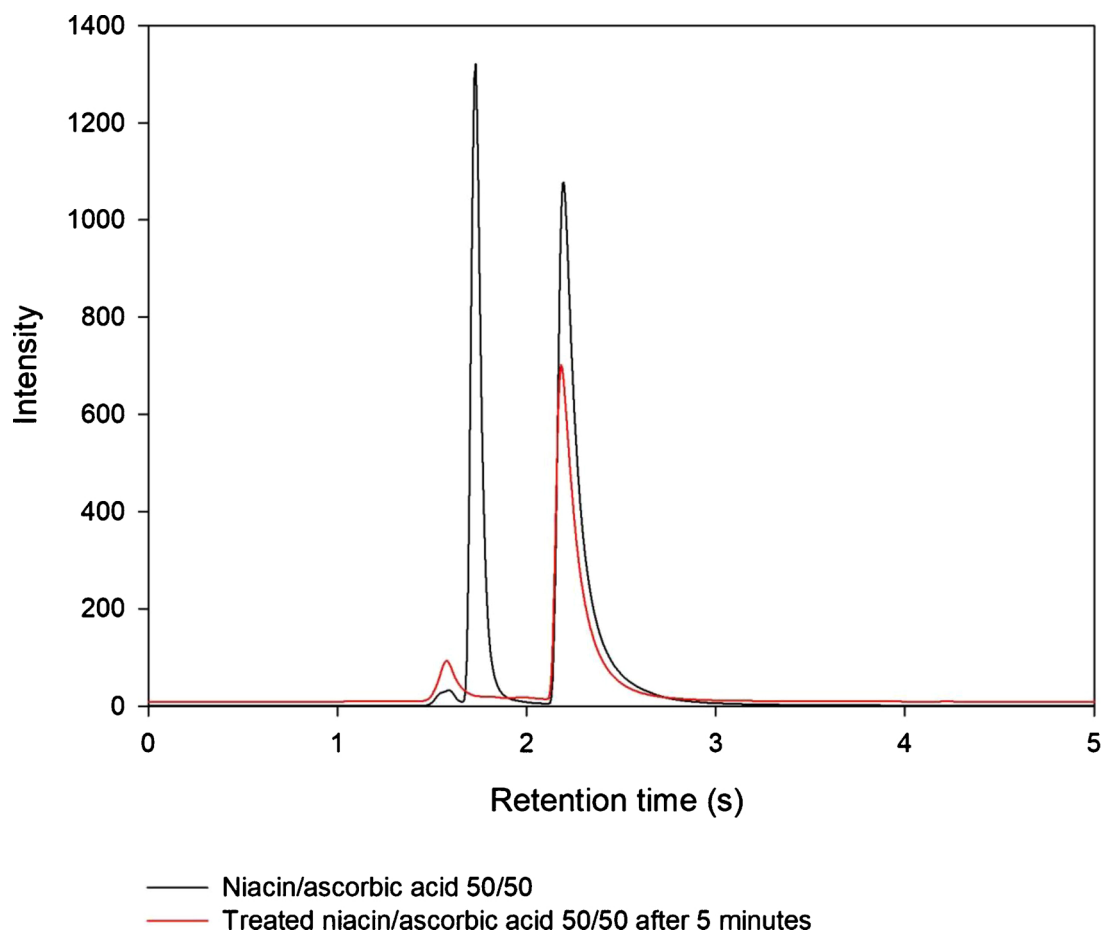


Fig. 19. Retention times profile for 50% niacin/ascorbic acid mixture, before and after the heating up to 190 °C and isotherm for 5 min.

parameter. Each investigated mixture shows at least a slight synergistic effect between the pure dusts the mixture is composed of, resulting in a deviation from the theoretical Le Chatelier Law trend. Niacin/anthraquinone and ascorbic acid/glucose mixtures exhibited slight synergistic behaviors of different nature. For niacin/anthraquinone mixtures, the physical synergistic effect lowers MITs values compared to that predicted by Le Chatelier Law. In the case of ascorbic acid/glucose mixtures, the physical-chemical synergistic behavior deviates both P_{Max} and K_{St} from ideality (Le Chatelier Law), with the highest deviation at 50% of glucose, where P_{Max} and K_{St} are equal to that of the most dangerous pure dust (ascorbic acid). Ascorbic acid/irganox 1222 and ascorbic acid/niacin mixtures shown strong synergistic behaviors that generated more severe conditions than in the case of pure dusts.

Based on the obtained results, we identified three mixtures safety classes (MSC):

- 1) no chemical-physical interaction, ideal behavior of the dusts, in agreement with Le Chatelier law (MSC 0);
- 2) physical-chemical interactions that affect the safety parameters of the mixture. However, the safety parameters belong to the variation range of that of pure dusts (MSC 1);
- 3) physical-chemical interactions that affect the safety parameters of the mixture (MSC 2).

In the case of behavior 2) the mixture exhibits a slight synergistic behavior leading to a deviation from the flammable/explosion parameters compared to that predicted by Le Chatelier Law. However, since those parameters values are equal or lower than those of the most dangerous pure dust, MSC 1 mixtures do not require stronger safety measures than that for the pure dusts.

In the case of behavior 3) the mixture exhibits a strong synergistic behavior eventually leading to a shift of the flammable/explosion parameters to more severe conditions than the pure dusts.

On this basis, we classified the dust mixtures studied in this work (Table 6).

5. Conclusions

Measurements of the flammable and explosion parameters of mixtures of flammable dusts (ascorbic acid/niacin; ascorbic acid/irganox, niacin/anthraquinone, ascorbic acid/glucose) show that these parameters are not the combination of the pure values and then it is not possible to predict *a priori* the behavior of the parameters of flammability and explosibility of the mixture. Significant physical-chemical interactions may arise among the powders, leading to unexpected and sometimes worse behaviors than those of pure compounds. From the DSC results, we may conclude that the physical interactions may be related to the formation of a eutectic point which reduces the temperature with respect to the pure dust at which melting and then boiling occur. DSC results combined with FTIR and HPLC analyses also show the possibility of chemical reactions that lead to the formation of volatiles, which contribute to the explosion phenomenon. On this basis, we propose a classification of mixture of dusts in three mixtures safety classes (MSC 0; MSC 1; MSC 2). In the case of both MSC 1 and MSC 2 mixtures, at least a slight synergistic behavior was found compared to the expected ideal behavior of dust mixtures. For MSC 2 mixtures, strong synergistic effects between pure dusts occur, resulting in more severe parameters than that of pure dusts. MSC 2 mixtures requires stronger safety measures than expected from the dangerous pure dust.

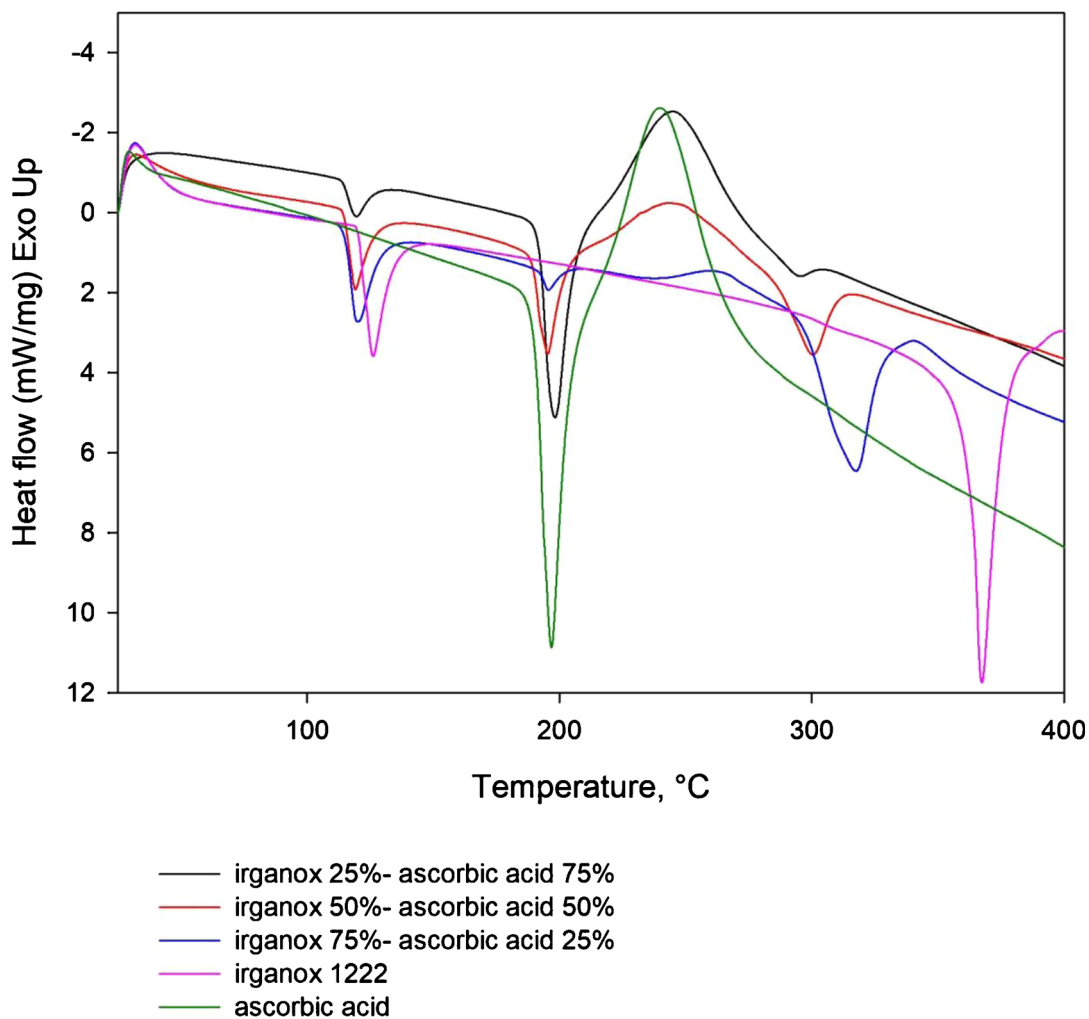


Fig. 20. Ascorbic acid–irganox 1222 mixtures DSC curves.

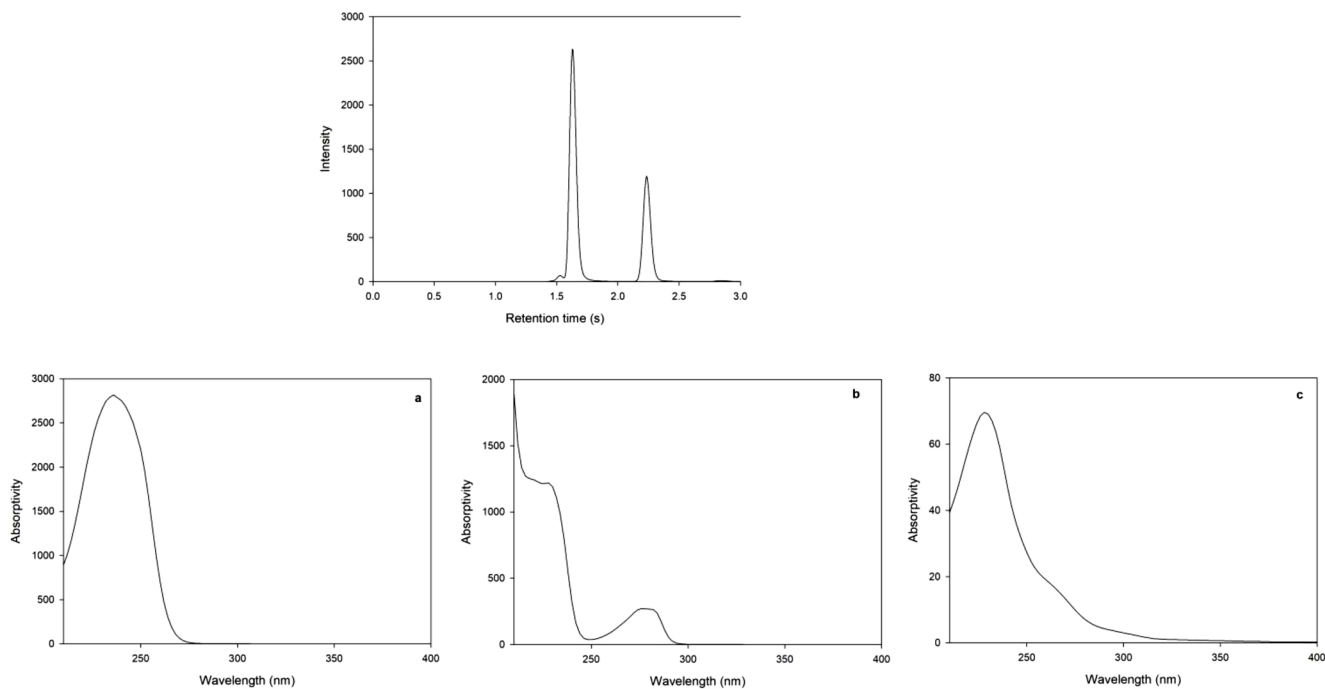


Fig. 21. Ascorbic acid (a), irganox 1222 (b) and ascorbic acid impurity (c) reference UV-spectra and retention time profile.

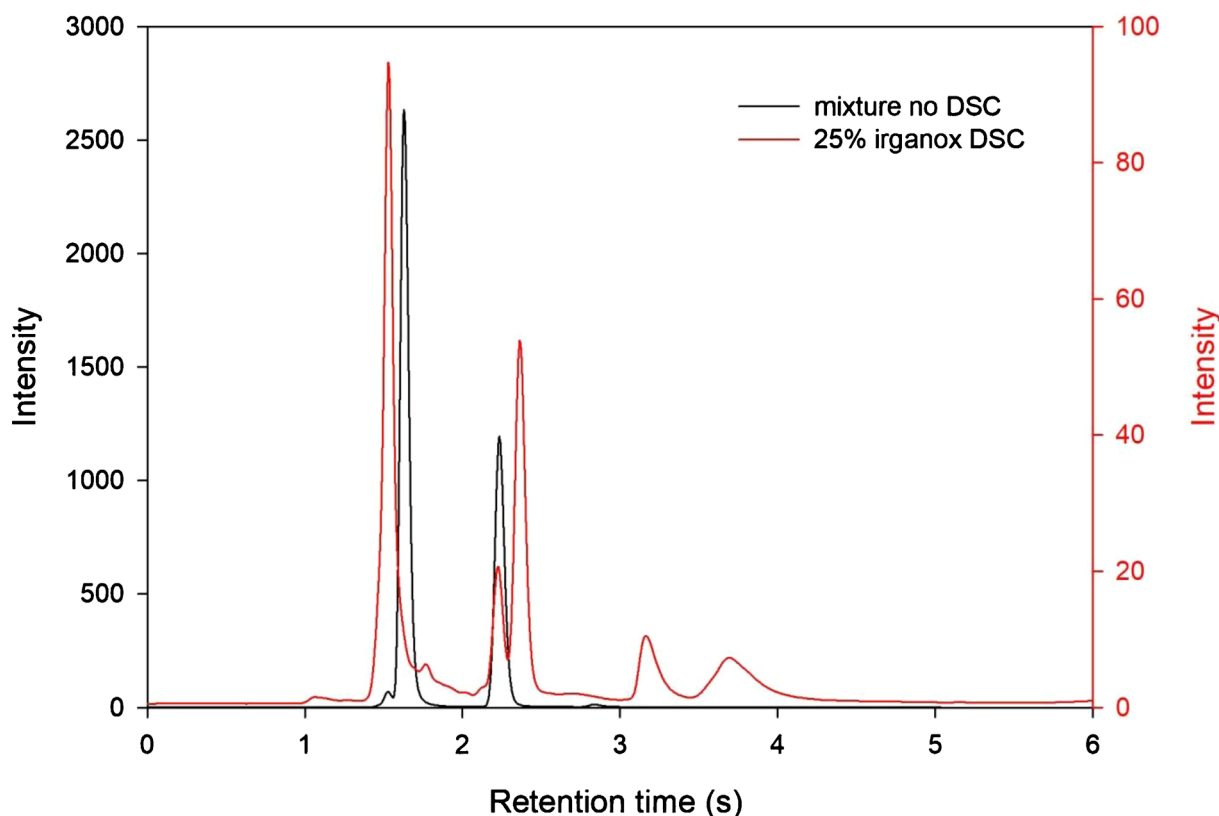


Fig. 22. Retention times profile for 25% irganox mixture.

Table 6
Classification of the mixtures.

Component	Class
Niacin-anthraquinone	MSC 1
Ascorbic acid-glucose	MSC 1
Ascorbic acid-irganox 1222	MSC 2
Ascorbic acid-niacin	MSC 2

CRedit authorship contribution statement

Luigi Centrella: Methodology. **Maria Portarapillo:** Methodology, Investigation, Writing - review & editing. **Giuseppina Luciani:** Methodology, Writing - review & editing. **Roberto Sanchirico:** Methodology, Writing - review & editing. **Almerinda Di Benedetto:** Conceptualization, Writing - review & editing, Supervision.

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.

Acknowledgments

Authors acknowledge Mr. Andrea Bizzarro for his excellent technical support.

References

Agilent Technologies Inc, 2003. Screening and Qualitative Identification of Antioxidant Polymer Additives by HPLC with UV/Vis and ApCI-MS Detection. Akkbi, M., Assim Bin, Z., Ahmad, F.B., 2011. Optimization and validation of RP-HPLC-UV/Vis method for determination phenolic compounds in several personal care

products. *Int. J. Anal. Chem.* 2011, 1–9. <https://doi.org/10.1155/2011/858153>.
 ASTM E1226-12a, 1988. Standard Test Method for Explosibility of Dust Clouds. ASTM Int., West Conshohocken, PA, pp. 1–13.
 ASTM E1491-06, 1991. Standard Test Method for Minimum Autoignition Temperature of Dust Clouds. ASTM Int., West Conshohocken, PA, pp. 1–10.
 ASTM E1515-14, 1993. Standard Test Method for Minimum Explosible Concentration of Combustible Dusts 1. ASTM Int., West Conshohocken, PA, pp. 1–9.
 ASTM E2019-03, 1999. Standard Test Method for Minimum Ignition Energy of a Dust Cloud in Air. ASTM Int., West Conshohocken, PA, pp. 1–9.
 ASTM E2021-15, 1999. Standard Test Method for Hot-Surface Ignition Temperature of Dust Layers. ASTM Int., West Conshohocken, PA, pp. 1–10.
 ASTM E2931-13, 2013. Standard Test Method for Limiting Oxygen (Oxidant) Concentration of Combustible. ASTM Int., West Conshohocken, PA, pp. 1–9.
 Bartknecht, W., 1989. *Dust Explosions: Course, Prevention, Protection*. Springer Verlag.
 Bartsch, N., Girard, M., Wilde, A., Bruhn, T., Kappenstein, O., Vieth, B., Hutzler, C., Luch, A., 2018. Thermal stability of polymer additives: comparison of decomposition models including oxidative pyrolysis. *J. Vinyl Add. Technol.* 25, E12–E27. <https://doi.org/10.1002/vnl.21654>.
 Cashdollar, K.L., 2000. Overview of dust explosibility characters. *J. Loss Prev. Process Ind.* 13, 183–199. [https://doi.org/10.1016/S0950-4230\(99\)00039-X](https://doi.org/10.1016/S0950-4230(99)00039-X).
 Di Benedetto, A., Garcia-Agreda, A., Dufaud, O., Khalili, I., Sanchirico, R., Cuervo, N., Perrin, L., Russo, P., 2011. Flame propagation of dust and gas-air mixtures in a tube. *Chia Laguna, Cagliari, Sardinia* 1, 11–13.
 Domalski, E.S., Hearing, E.D., 1996. Heat capacities and entropies of organic compounds in the condensed phase. Volume III. *J. Phys. Chem. Ref. Data* 25, 1–525. <https://doi.org/10.1063/1.555985>.
 Eckhoff, R.K., 2003. *Dust Explosions in the Process Industries*, 3rd edition. Gulf Professional Publishing.
 Fan, X., 2005. Formation of furan from carbohydrates and ascorbic acid following exposure to ionizing radiation and thermal processing. *J. Agric. Food Chem.* 53, 7826–7831. <https://doi.org/10.1021/jf051135x>.
 Garcia-Agreda, A., Di Benedetto, A., Russo, P., Salzano, E., Sanchirico, R., 2011. Dust/gas mixtures explosion regimes. *Powder Technol.* 205, 81–86. <https://doi.org/10.1016/j.powtec.2010.08.069>.
 International section for the Chemical Industry, 2003. *Dust Explosions- Protection Against Explosions Due to Flammable Dusts*.
 Jingyan, S., Yuwen, L., Zhiyong, W., Cunxin, W., 2013. Investigation of thermal decomposition of ascorbic acid by TG-FTIR and thermal kinetics analysis. *J. Pharm. Biomed. Anal.* 77, 116–119. <https://doi.org/10.1016/j.jpba.2013.01.018>.
 Li, Q., Lin, B., Dai, H., Zhao, S., 2012. Explosion characteristics of H₂/CH₄/air and CH₄/coal dust/air mixtures. *Powder Technol.* 229, 222–228. <https://doi.org/10.1016/j.powtec.2012.06.036>.
 Limacher, A., Kerler, J., Conde-Petit, B., Blank, I., 2007. Formation of furan and methylfuran from ascorbic acid in model systems and food. *Food Addit. Contam.* 24,

- 122–135. <https://doi.org/10.1080/02652030701393112>.
- Marmo, L., 2010. Case study of a nylon fibre explosion: an example of explosion risk in a textile plant. *J. Loss Prev. Process Ind.* 23, 106–111. <https://doi.org/10.1016/j.jlp.2009.06.006>.
- Marmo, L., Sanchirico, R., Di Benedetto, A., Di Sarli, V., Riccio, D., Danzi, E., 2018. Study of the explosible properties of textile dusts. *J. Loss Prev. Process Ind.* 54, 110–122. <https://doi.org/10.1016/j.jlp.2018.03.003>.
- NIST Standard Reference Database 69: NIST Chemistry WebBook, 2018.
- Portarapillo, M., Luciani, G., Sanchirico, R., Di Benedetto, A., 2020. Ignition mechanism of flammable dust and dust mixtures: an insight through TG/DSC analysis. *AIChE J.* <https://doi.org/10.1002/aic.16256>.
- Royal Society of Chemistry, 2020. ChemSpider - Search and Share Chemistry.
- Russo, P., Di Benedetto, A., 2013. Review of a dust explosion modeling. *Chem. Eng. Trans.* 31, 955–960. <https://doi.org/10.3303/CET1331160>.
- Russo, P., Di Benedetto, A., Sanchirico, R., 2012. Theoretical evaluation of the explosion regimes of hybrid mixtures. *Chem. Eng.* 26, 51–56. <https://doi.org/10.3303/CET1226009>.
- Russo, P., Amyotte, P.R., Khan, F.I., Di Benedetto, A., 2013. Modelling of the effect of size on flocculent dust explosions. *J. Loss Prev. Process Ind.* 26, 1634–1638. <https://doi.org/10.1016/j.jlp.2013.07.012>.
- Salatino, P., Di Benedetto, A., Chirone, R., Salzano, E., Sanchirico, R., 2012. Analysis of an explosion in a wool-processing plant. *Ind. Eng. Chem. Res.* 51, 7713–7718. <https://doi.org/10.1021/ie2023614>.
- Sanchirico, R., Di Sarli, V., Di Benedetto, A., 2018. Volatile point of dust mixtures and hybrid mixtures. *J. Loss Prev. Process Ind.* 56, 370–377. <https://doi.org/10.1016/j.jlp.2018.09.014>.
- Saunier, J., Herry, J.M., Yagoubi, N., Marlière, C., 2017. Exploring complex transitions between polymorphs on a small scale by coupling AFM, FTIR and DSC: the case of Irganox 1076® antioxidant. *RSC Adv.* 7, 3804–3818. <https://doi.org/10.1039/c6ra25632e>.
- Wiercigroch, E., Szafraniec, E., Czamara, K., Pacia, M.Z., Majzner, K., Kochan, K., Kaczor, A., Baranska, M., Malek, K., 2017. Raman and infrared spectroscopy of carbohydrates: a review. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 185, 317–335. <https://doi.org/10.1016/j.saa.2017.05.045>.
- Worsfold, S.M., Amyotte, P.R., Khan, F.I., Dastidar, A.G., Eckhoff, R.K., 2012. Review of the explosibility of nontraditional dusts. *Ind. Eng. Chem. Res.* 51, 7651–7655. <https://doi.org/10.1021/ie201614b>.