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Long-term assessment of the thermal stability of sodium nitrate-urea eutectic phase change material

Laura Quant [a,*], Gonzalo Diarce [b], Lourdes Bouzas [a], Jean-Pierre Bédécarrats [c], Ana García-Romero [a]

[a] ENEDI Research Group, Dpto. de Ingeniería Minera, Metalúrgica y de Ciencia de los Materiales, Escuela de Ingeniería de Bilbao, University of the Basque Country - UPV/EHU, Rafael Moreno Pitxitxi 2, 48103, Bilbao, Spain
[b] ENEDI Research Group, Dpto. de Ingeniería Energética, Escuela de Ingeniería de Bilbao, University of the Basque Country - UPV/EHU, Rafael Moreno Pitxitxi 2, 48103, Bilbao, Spain
[c] Université de Pau et des Pays de l'Adour/ E2S UPPA, Laboratoire de Thermique, Énergétique et Procédés - IPRA, EA1932, Pau, 64000, France

A B S T R A C T

The eutectic mixture formed by urea and sodium nitrate can be an interesting candidate for use as a phase change material for thermal energy storage in space heating and domestic hot water applications. It shows a melting point of 85 °C, a melting enthalpy of 172 J/g and a price around 0.9 €/kg. However, the thermal stability of the mixture is a great concern for this application. A preliminary evaluation of the thermal stability was performed and previously reported by the authors. It consisted of an accelerated thermal cycling test with 210 thermal cycles and the material showed a stable behavior. Nevertheless, the long-term stability of urea in the liquid state at temperatures below 100 °C is uncertain and requires a specific study. The main objective of the present work is to evaluate the long-term thermal stability of the mixture when it is exposed to long periods of use under conditions representative of actual applications, by means of analyzing the thermal and compositional behavior of samples remaining at 100 °C for several periods up to one year. A methodology is proposed, which intends to isolate the thermal degradation phenomenon from others, such as phase segregation, supercooling, and polymorphism, that can be introduced by thermal-cycling. It also aims to be more representative of the actual application than the accelerated thermal cycling approach.

1. Introduction

Thermal energy storage (TES) plays an important role in energy efficient systems because it enables the decoupling of thermal energy production and demand. Latent heat thermal energy storage (LHTES) systems are based on phase change materials (PCM), which store energy via the solid-liquid phase transition [1]. Heat is stored when the material melts and is subsequently released by its solidification. These systems have been widely researched because they usually display greater energy storage densities compared to sensible heat storage; however, research is still required to develop economically competitive PCMs with increased storage capacities.

The eutectic mixture, consisting of 71.25 wt% urea ($CO(NH_2)_2$) and 28.75 wt% sodium nitrate ($NaNO_3$), has a melting point of 85 °C, which is within the temperature range suitable for domestic hot water (DHW) and space heating applications in buildings. The mixture shows several interesting characteristics as a PCM, such as high melting energy density, affordable price, widespread availability and biodegradability (its main use is for soil fertilization) [2,3]. The use of pure urea as PCM for thermal energy storage around 132 °C (its melting point) was investigated several decades ago [4–10], but it was discarded due to its low thermal stability: liquid urea degrades rapidly into different compounds. In this context, no other studies have been carried out to date that attempt to prevent or eliminate degradation or improve thermal stability. However, as the eutectic mixture of urea and sodium nitrate has a significantly lower melting point than pure urea (85 vs 132 °C), the rate of degradation could be significantly reduced and thermal degradation would become a disadvantage rather than a limiting factor.

Consequently, in previous works by the authors [2,3], a detailed study of the urea-sodium nitrate system for its use as a PCM was performed. The research included the determination of its phase diagram, the main thermo-physical properties and an accelerated thermal cycling.

It was concluded that the mixture can be considered a good candidate for use as a PCM. However, the performed accelerated thermal cycling is a preliminary test suitable to discard materials with poor thermal stability, but it does not describe the actual long term PCM stability/degradation behavior. Therefore, long-term stability and degradation studies should be carried out to confirm the potential of the mixture.

In order to investigate the long-term thermal stability of PCMs, the reaction pathway that the high temperature exposure could produce has to be assessed. The degradation kinetics of pure urea and pure sodium nitrate have been reported separately in the literature. Regarding sodium nitrate degradation, the literature [11–13] indicates that it is stable up to 350 °C (above its melting temperature of 308 °C) and slightly decomposes up to 450 °C. Therefore, the decomposition of sodium nitrate below 100 °C is foreseen to be negligible. As a result, only the decomposition of urea in the urea-sodium nitrate mixture requires consideration.

Pure urea degradation has been studied for its role as an ammonia precursor in automotive selective catalytic reduction for the removal of nitrogen oxides in exhaust gases [14–21] and as a degradation product of urea nitrate ($CH_5N_3O_4$) thermolysis [22,23]. The main degradation pathway of urea is shown in Fig. 1.

According to the literature, when exposed to high temperatures, urea decomposes in a first stage into ammonia and isocyanic acid. Then, isocyanic acid reacts with unreacted urea to produce biuret. Afterwards, cyanuric acid can form due to the reaction of biuret with isocyanic acid. These reactions take place in the absence of water. In a humid atmosphere, isocyanic acid reacts with water, causing more ammonia and carbon dioxide. Evidence indicates that the presence of water promotes higher degradation rates [18]. In addition to the mentioned decomposition products, other compounds might arise when urea is heated to very high temperatures under various conditions, such as amelide, ameline and melamine, which are formed by polymerization, and/or anions such as cyanurates, isocyanates, acetates, formats, nitrates and nitrites [20].

However, most of the published works dealing with urea thermolysis analyze the process at temperatures higher than the intended operating temperature range of the urea-sodium nitrate eutectic mixture as a PCM (<100 °C). Only a few works ([14,22]) assess the degradation of urea at temperatures as low as 100 °C (below the melting point of pure urea). Furthermore, degradation has generally been studied under conditions other than those designed for TES (open container, catalysts, solid-/dissolved urea in water, etc.). For this reason, these studies cannot be considered representative of the mixture behavior in the working conditions as a PCM. In fact, most of the published research concerning urea thermolysis ultimately seeks to achieve the maximum conversion of urea into ammonia, which is the opposite objective of the present study.

Therefore, based on the presented state-of-the-art, this article studies the long-term thermal stability of the urea-sodium nitrate eutectic mixture to determine its suitability as a PCM. The study includes holding molten samples at a defined temperature for soaking periods ranging from one day to one year and subsequently analyzing the thermal and compositional variations using various analytical techniques.

In addition, it is intended to provide methodological guidelines for the development of reliable methods to study the long-term degradation of PCMs. During the last decade, the discovery of new PCMs has been an important objective of research into latent heat energy storage [24], which has led to the use of fast methods to discard materials with poor thermal stability [25]. However, the typically employed methods do not isolate the thermal degradation problem from other parameters that could act together, such as phase segregation, crystallization problems, supercooling, etc.

Indeed, ongoing research has revealed that the involved mixture shows phase segregation upon thermal cycling. Phase segregation occurs in mixture-based PCMs and usually depends on the cooling rate, supercooling (if any), or on the different densities of the pristine materials that form the mixture. Conversely, thermal degradation normally depends on the maximum operation temperature, system tightness, surrounding atmosphere and others. Since both effects are caused by different reasons, the potential solutions for each effect should also be different. Therefore, it is essential to isolate the two effects in order to properly evaluate the long-term stability of a PCM on the one hand, and the causes and solutions to deal with phase segregation on the other.

Accordingly, the development of reliable methods to study PCM degradation is one of the focuses of the international community's research work in this field [26], and it is a secondary objective of the present article.

2. Materials and methods

The thermal degradation procedure followed consists of placing several samples of the eutectic mixture inside a heating cabinet at 100 °C where they remained for periods ranging from 1 day to 1 year (370 days). Afterwards, their main thermal properties were determined by differential scanning calorimetry (DSC). Selected samples were also analyzed by high performance liquid chromatography (HPLC), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

Before the methods are detailed, it is convenient to remark that the ongoing research evidenced that phase segregation became significant upon thermal cycling of large volume samples, while it became negligible when samples were not thermally cycled. It is also well known that
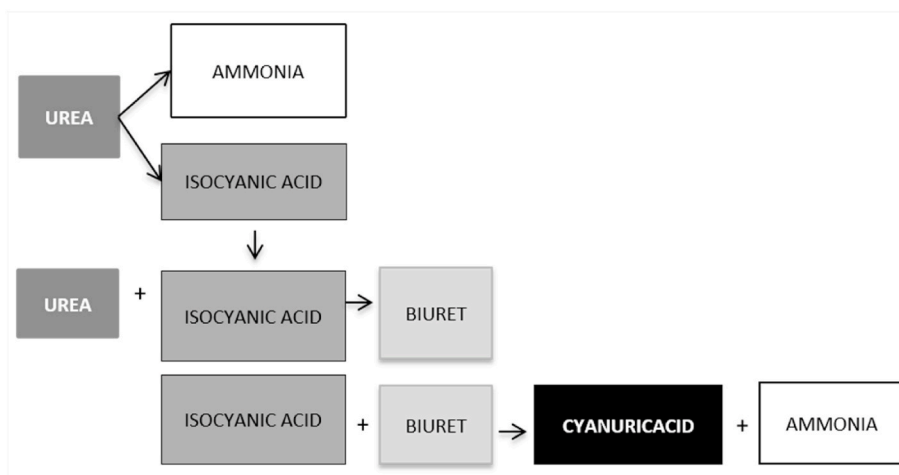

Fig. 1. Main urea degradation pathway.

small samples, such as DSC crucibles (20–100 μL), minimize phase segregation [3]. Since this article focuses on thermal degradation, DSC crucibles were used as sample containers. Furthermore, no melting/solidification cycles were performed. In this way, any potential phase segregation was avoided. The study of the phase segregation of the urea-sodium nitrate eutectic mixture, along with the supercooling, will be reported in forthcoming articles.

2.1. Materials and sample preparation

For thermal degradation, the samples consisted of DSC closed crucibles with a dry mixture of 71.25 wt% urea and 28.75 wt% sodium nitrate (hereafter called U-SN eutectic mixture). They were prepared following a specific procedure to prevent moisture uptake, due to its possible influence on the urea degradation process. Table 1 gathers the main characteristics of the raw materials used, while details of the relevant instruments used for sample preparation are given in Table 2. Sample preparation is described next.

First, the pure powdered reagents were introduced into a glass vial, to a total of 4 g of the eutectic mixture. A magnetic stirrer was introduced into the vial, which was hermetically sealed with a screw cap. To melt the material and produce the eutectic mixture, the vial was immersed in a glycerin bath with magnetic stirring at 90 °C for 30 min. Then, 20 μl of the melted material was poured into a DSC crucible with the aid of a micropipette. The crucibles with the PCM were placed (still open) in a desiccator containing phosphorus pentoxide as a drying agent for 3 days. The inner atmosphere had a relative humidity of 7% and room temperature. The water content of several selected samples was measured after this process by means of Karl Fisher titration [27]. All samples showed a water content of less than 0.1%.

The desiccator was then opened inside a glove box with a controlled humidity atmosphere (16% relative humidity), where the DSC crucibles were sealed. Finally, the sealed crucibles were weighed on a 0.1 mg resolution scale.

Stainless steel DSC crucibles for medium pressure were used, with PCTFE O-ring sealing joints to maximize gas-tightness. The PCTFE O-rings were selected as they are impermeable to gaseous ammonia, which is a forecast by-product of urea decomposition.

Three samples were prepared for each degradation time, making a total of 48 samples.

2.2. Thermal degradation procedure

The sealed crucibles were placed into a heating cabinet (J.P. Selecta, model 2000210) at 100 °C (± 1.5 °C) for a predefined exposure time (from 1 day to 1 year). The crucibles were placed onto an aluminum flat tray to provide a homogeneous temperature to all (see Fig. 2). After the set-time elapsed, the corresponding crucibles were removed from the oven and placed in a desiccator for 30 min. They were then weighed to record any variation in sample mass.

2.3. Analytical procedure and techniques

The degraded samples were analyzed by different techniques: DSC was used to determine the evolution of the melting temperature and the melting enthalpy over an increasing degradation time. HPLC, XRD and FTIR were employed to obtain information concerning the composition of the degraded samples and to attain a better understanding of the

Table 1
Raw materials employed for the sample preparation.

Material	Supplier	Purity	Quality
Urea	Panreac Química S.L.U.	99%	Laboratory grade
Sodium nitrate	Panreac Química S.L.U.	99%	
Phosphorus pentoxide	Panreac Química S.L.U.	98%	

Table 2
Equipment used for the sample preparation.

Equipment	Brand	Model
Laboratory scale	Ohaus	Discovery 114C
Gas-tight DSC crucibles	Mettler Toledo	Medium pressure stainless steel crucibles with PCTFE O-rings
Micropipete	Rainin by Mettler Toledo	Pipet-Lite XLS monocanal
Glove box	Plas-Labs, Inc.	330 ABB
Karl Fischer coulometric Tritration	Mitsubishi Chemical	KF-31

Fig. 2. Sample rack with some of the samples inside the heating cabinet.

mixture's thermal degradation. Table 3 sets out the equipment used. The methodology used for the DSC, XRD and HPLC measurements was previously described in detail in Ref. [2]. However, a summary of the most important details is provided below.

2.3.1. Differential scanning calorimetry (DSC)

The temperature program used is shown in Fig. 3. It consists of two heating segments and one cooling segment. The first heating ramp was intended to settle the sample at the bottom of the crucible to achieve good contact. Both the heating and cooling rates were 1 °C/min, and the isothermal segments lasted 10 min on each side of the dynamic segments.

To analyze the results, the onset and peak temperatures, the latent heat and the total enthalpy variation in the temperature range of 60 to 95 °C were determined in the cooling segment and in the second heating segment. The total enthalpy variation was determined (see Fig. 4) by measuring the area (*a*) corresponding to the latent enthalpy and the addition of the area (*b*), which accounts for the sensible heat. In some samples, new peaks or artifacts different from the eutectic melting characteristics were found, so they were registered for later analysis.

In some of the samples with a prolonged degradation, crystallization did not occur completely during the cooling ramp. In these cases, the DSC tests were repeated using a heating and cooling rate of 0.5 °C/min.

Table 3
Analytical techniques used for the characterization of degraded samples.

| Analytical technique	Brand	Model
Differential Scanning Calorimetry (DSC)	Mettler Toledo	DSC1
High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS)	Agilent Technologies	1200 Series
X Ray Diffraction (XRD)	Philips	X'pert Pro
Powder Diffraction File (PDF) database	–	–
XRD data treatment software	PANalytical	X'pert HighScore
Fourier-Transform Infrared Spectroscopy (FTIR)	Jasco	4200
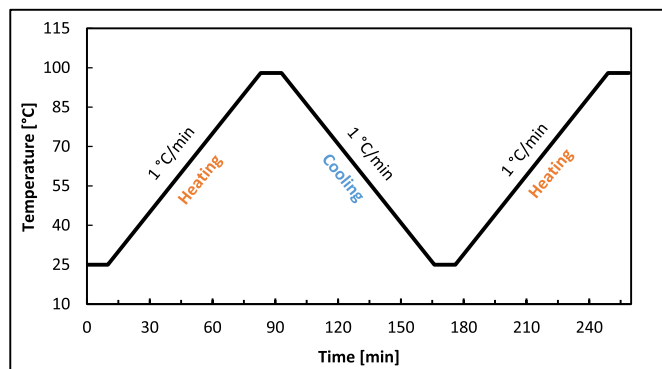
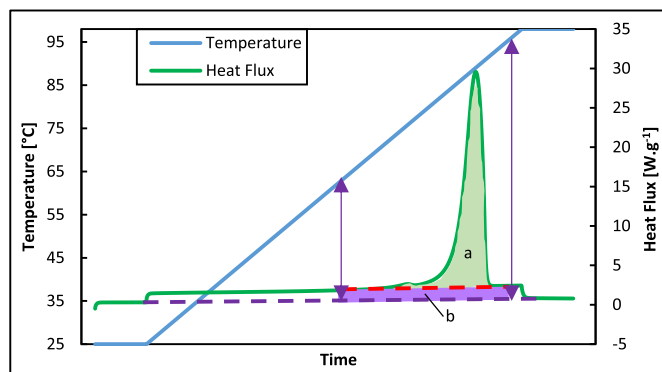**Fig. 3.** DSC temperature program.

Fig. 4. Determination of total enthalpy variation. Area "a" corresponds to the melting enthalpy and area "b" corresponds to the sensible enthalpy in the temperature range from 60 to 95 °C.

2.3.2. High performance liquid chromatography (HPLC)

Selected samples were submitted to HPLC analysis in order to quantify the content of urea and potential non-gaseous by-products in the degraded samples. The column used was a SeQuant® ZIC- HILIC 3.5 mm/150 × 4.6 mm. Monitoring of the urea and its expected potential degradation byproducts (biuret and cyanuric acid) was performed using a triple quadrupole mass spectrometer equipped with an electrospray ionization interface. To quantify the compounds, calibration curves were prepared using various solutions of each pristine compound (urea, biuret and cyanuric acid) with different concentrations. The calibration curves were fitted by linear regression, obtaining a correlation coefficient greater than 0.996 in all cases.

To prepare each HPLC sample, the PCM mass (about 30 mg) to be analyzed was extracted from the corresponding DSC crucible and ground by hand in an agate mortar to get a homogeneous powder. Next, approximately 10 mg of each sample were dissolved in 25 ml of distilled water. This solution was subsequently diluted with distilled water to 1/100 and 1/50 ml/ml respectively. A volume of 5 μL of the diluted samples were injected into the HPLC-MS for the chromatographic analysis. Two samples of the 1/100 dilutions and one sample of the 1/50 dilution were measured for each of the thermally tested samples.

All the analyzed samples were specifically analyzed to identify any trace of urea, biuret and cyanuric acid. However, those samples degraded for 180 days were subjected to a broader scanning, in order to determine any presence of additional degradation compounds.

Note that, unlike DSC, this technique is appropriate to distinguish between phase segregation and thermal degradation, due to the mass quantification of the compounds. A potential phase segregation without thermal degradation would render results with a composition equal to a non-degraded sample. Conversely, by DSC, it would be difficult to distinguish between the two effects.

2.3.3. X-ray diffraction (XRD)

X-ray diffraction was used to determine the crystalline phases in the samples. The samples degraded for different exposure times were X-ray diffracted and the evolution of the diffraction patterns was recorded. It is worth remembering that this technique is able to determine the composition and crystallographic nature of the crystalline materials, but does not determine the composition of any amorphous compound that could have formed.

In a previous article by the authors [2], it was determined that the U-SN eutectic mixture could form a metastable phase, different from urea and sodium nitrate. This phase has not been reported in the literature, so its diffraction patterns are unavailable in the used XRD patterns database (see Table 3). Consequently, all analyzed samples were annealed to obtain the equilibrium phases and to allow the identification of possible by-products that appear in the samples degraded over time. The annealing heat treatment consisted in holding the samples at 80 °C for 10 h.

After the annealing, all the material contained in the DSC crucible (about 30 mg) was extracted, ground by hand in an agate mortar to obtain a fine and homogeneous powder and placed on sample carriers for XRD analysis.

2.3.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR was used as a complementary technique to determine the composition of the samples by determining their infrared spectra. The technique provides information on the composition of the samples, including new compounds that could have formed after degradation, which may be non-crystalline. The KBr tablet technique was employed, as it is the most usual methodology for the analysis of powdered samples. It was in transmittance mode, using a disc or tablet of potassium bromide (KBr, spectroscopic purity).

The U-SN samples were extracted from the crucibles and ground with an agate mortar. Tablets were prepared by mixing the powdered solid samples (about 10 mg) with KBr powder (approximately 300 mg). This mixture was ground again and transferred to an IR tablet mold and placed in a hydraulic press. A pressure of 10 tons was applied for 3 min to obtain a KBr disc in which the sample was homogeneously distributed. Afterwards, the infrared spectra was obtained in the 400 to 4000 cm⁻¹ region following the standard procedure, with a spectral resolution of 4 cm⁻¹ and accumulating 40 scans to obtain a good signal-to-noise ratio.

Pure urea and sodium nitrate samples were first analyzed in order to obtain the spectra of the pristine components. Then 5 U-SN eutectic mixture samples were analyzed, corresponding to three different treatment times: 0 days, 40 days, 120 days, 270 days and 370 days.

3. Results

This section presents the main experimental results of the thermal stability study. The discussion of the analysis of the mass-loss, DSC, HPLC and XRD results is presented in Section 4.

3.1. Mass-loss

The crucibles used in the study were selected for their gas tightness according to the supplier's specifications, which indicated a maximum allowable pressure of 2 MPa (20 bars) and a maximum working temperature <220 °C, both significantly above the operating conditions in this study. However, every sample was weighed before and after the thermal treatment and mass variations were noticed.

The evolution of mass-loss is shown in Fig. 5. After 370 days, the crucibles show an average mass decrease of 2.2%. The mass-loss trend increases over time, but the initial stage does not follow a linear trend. Discussion of these results is extended in Section 4.
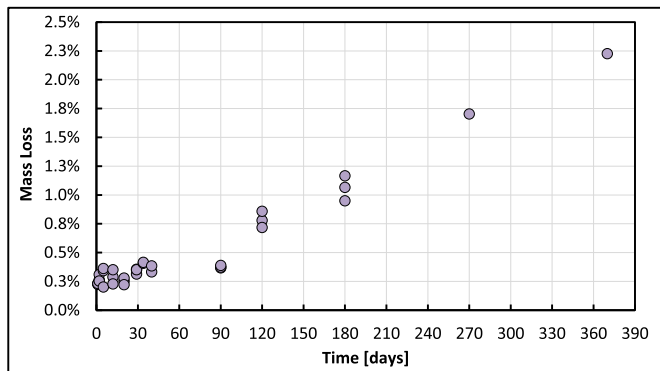
Fig. 5. Evolution of the average mass loss over time.

3.2. Differential scanning calorimetry (DSC)

The thermal properties of the samples were measured by DSC. Fig. 6 shows the thermograms of selected samples degraded during a different period of time. All the thermograms were analyzed taking into account the evolution of the curve outline: the melting and solidification peaks and any other unexpected peak or artifact.

The general evolution of the melting signal with increasing thermal treatment time shows a tendency for the main endothermic peak to move towards lower onset and peak temperatures. In addition, the peaks become wider and there is a reduction of the melting enthalpy and the total variation of enthalpy in the temperature range of 60–95 °C.

Some of the degraded samples showed a small peak when heated, at around 74 °C, before the melting signal. This secondary peak formed in some samples during the first 90 days at 100 °C. The existence of two peaks in the thermograms suggests that two phases are present or that the samples no longer show a single melting point but a semi-solid interval. These two signals may have overlapped, forming a large single peak, in samples exposed to a longer degradation time, where the melting peak widens and the starting temperature drops from the initial 85 °C to as low as 75 °C.

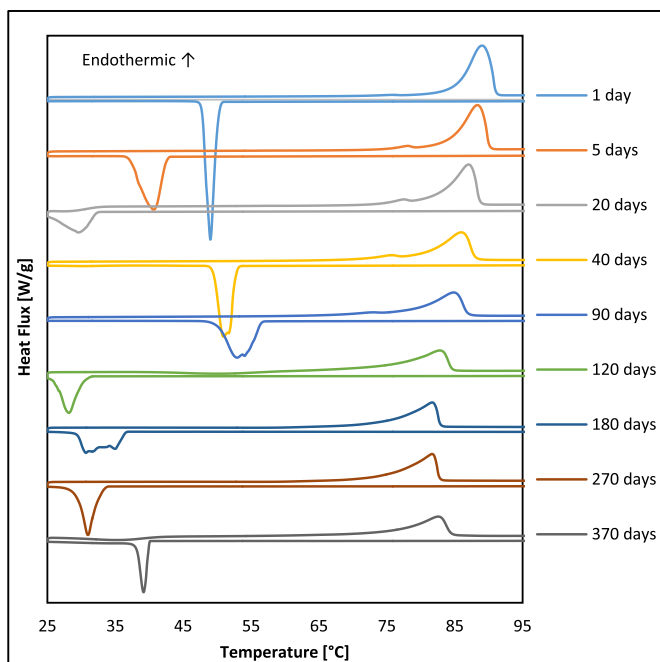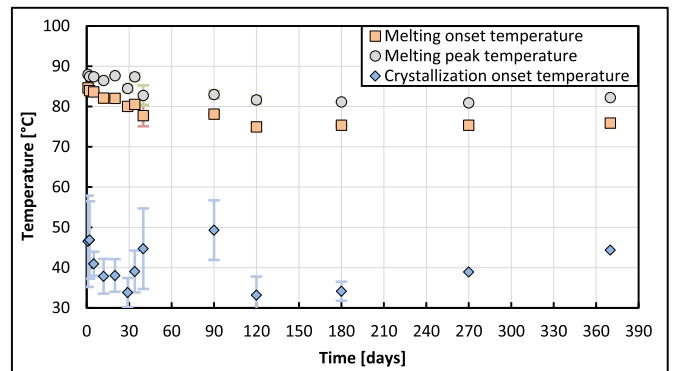Figs. 7 and 8 show the evolution of the average melting onset and

Fig. 7. Evolution of the onset and peak temperatures during heating and of the onset temperatures on cooling; standard deviation is also included.
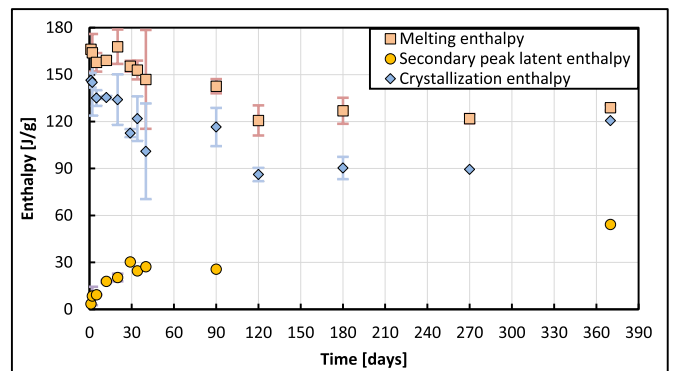

Fig. 8. Evolution of the measured average melting and crystallization enthalpies (main peaks), and the average melting enthalpy measured in the secondary peak formed on some samples. Each point corresponds to the average of three samples measured at the same time. The bars represent the standard deviation.

peak temperatures and the latent melting and crystallization enthalpies, as well as their standard deviation. These values decrease in the first 40 days of exposure to 100 °C. Afterwards, they remain stable at a melting enthalpy of 120–130 J/g and a melting onset temperature of around 75 °C until 370 days have elapsed, which is the maximum residence time tested in the study.

The large supercooling that occurs during crystallization shows the typical scattering of stochastic nature when small samples are used [28, 29]. However, the scattering is almost negligible in samples degraded longer than 120 days, as shown in Fig. 7. This may indicate a compositional change in the system. In all cases, the crystallization enthalpy is lower than the melting enthalpy. This well known phenomenon is due to the recalescence that occurs after supercooling, where part of the latent heat is used to heat up the sample itself. The analysis of this phenomenon is beyond the scope of this paper.

Table 4 shows a comparison between the average values (three samples) obtained for the original (non-degraded) mixture and the value corresponding to the samples held at 100 °C for 370 days. The properties

Fig. 6. Evolution of thermograms with increasing degradation time (selected samples).

Table 4
Main thermal characteristics of the U-SN eutectic mixture: non-degraded and after 370 days at 100 °C (average values of three samples).

Measured property	Non-degraded mixture	After 370 days at 100 °C	% Loss
Avg. onset temperature [°C]	84.63	75.91	10%
Avg. peak temperature [°C]	87.97	82.22	7%
Avg. latent heat [J/g]	168.94	128.82	24%
Avg. latent + sensible heat (60–95 °C) [J/g]	238.18	189.74	20%

included are: onset temperature, peak temperature, latent heat and latent heat plus the sensible heat in the 60 to 95 °C temperature range. The melting enthalpy loss is lower than 25% and is reduced to 20% for the case of total enthalpy change.

3.3. High performance liquid chromatography (HPLC)

HPLC was used to identify and quantify the urea and degradation products present in the samples. Figs. 9 and 10 show the evolution of the mixture's composition regarding the content of urea, biuret and cyanuric acid. Each value corresponds to one sample (not to the average of several samples). The values shown in the graphs were normalized, taking into account the urea percentage in the non-degraded samples. This means that the original mixture corresponding to the eutectic composition (where urea corresponds to 71.25% of the total mass) is considered as 100% urea for the degradation study.

All the analyzed samples contained urea in a large proportion. In samples from 1 to 40 days, the urea content decreased (irregularly) from 100% to 88%. Afterwards, a clear stabilization trend is observed and the urea composition remained (quasi) constant over time.

The presence of biuret was also detected in all samples. However, its percentage in the samples remained below 5% (from the original urea content) in samples of all the thermal exposure periods. Its evolution showed an initial increase, reached a maximum of 5% in samples around 120 days and decreased afterwards.

Regarding cyanuric acid, it was solely detected in the samples degraded for more than 40 days, always in very small quantities (below 3.5%, calculated from the original urea content). Its presence increased in those samples tested for 120 days and longer, which coincides with the decrease in biuret. This is in agreement with the degradation reaction of urea, and will be discussed in detail in Section 4.

A broader scanning to identify the presence of additional degradation products was performed in selected samples. No traces of different compounds were detected.

3.4. X-ray diffraction (XRD)

Samples exposed at 100 °C for different selected times were analyzed by XRD to identify the crystalline phases. In order to evaluate the XRD results, a semi-quantitative analysis was carried out by comparing the intensity of the measured peaks with the reference intensity ratio (RIR) from the PDF database, using the Xpert High Score software (see Table 3). This procedure presents an uncertainty as large as 10% in terms of quantification; however, it is a powerful tool to determine changes in the crystallographic nature of the compounds.

First, a non-degraded sample of the U-SN eutectic mixture was analyzed. Its diffraction pattern is shown in Fig. 11. Diffraction peaks according to the database are marked by vertical lines of different colors:
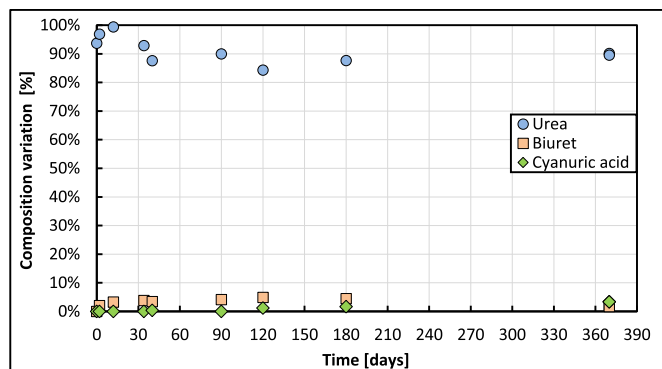

Fig. 9. Evolution of urea, biuret and cyanuric acid content in the selected samples measured by HPLC. Biuret and cyauric acid values representation are enlarged in Fig. 10.
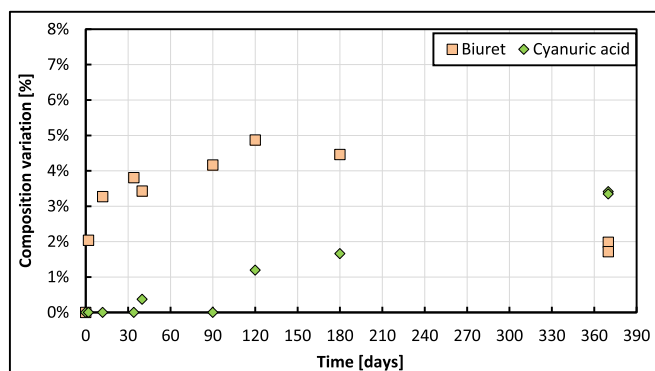

Fig. 10. Evolution of biuret and cyanuric acid content in the selected samples.
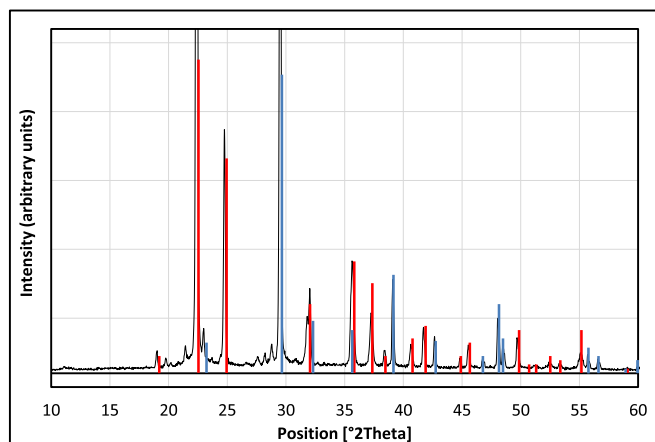

Fig. 11. Diffraction pattern of a non-degraded sample (the blue lines correspond to the position of the sodium nitrate peaks and the red lines to those of urea). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

red peaks correspond to pure urea and blue peaks to pure sodium nitrate. All the main diffraction peaks determined in the diffracted samples match the diffraction of either pure urea or pure sodium nitrate. This confirms that the non-degraded sample is mostly formed by a eutectic mixture of the pristine materials. Some minor intensity peaks that correspond to neither urea nor sodium nitrate were also observed. They do not match any foreseen degradation compound, but do match the metastable form previously identified by the authors in Ref. [2] and described in Section 3.1.5.

Fig. 12 shows the evolution of the diffraction patterns over the degradation testing time, between 10° and 60° (2Theta), where the most significant diffraction peaks are expected. The results of all degraded samples show the highest intensity peaks in the same 2Theta positions. There are no evident changes in these peaks with longer degradation times. The analysis of the diffraction patterns indicates that the urea/sodium nitrate proportion in all the degraded samples remained at approximately 70–80% urea and 20–30% sodium nitrate, close to the original eutectic composition: 71.25 wt% urea and 28.75 wt% sodium nitrate.

However, there are small (but significant) intensity-proportionality changes between the urea and the sodium nitrate peaks that point towards a certain decrease in the urea content. Fig. 13 *a*) shows the diffraction signals in the 2Theta positions from 31 to 33°, where two peaks are shown, one corresponding to urea and the other to sodium nitrate. Fig. 13 *b*) shows the evolution of the relative intensity ratio of these two peaks over the testing time. It can be appreciated that the intensity ratio gradually decreases from the fresh sample until the
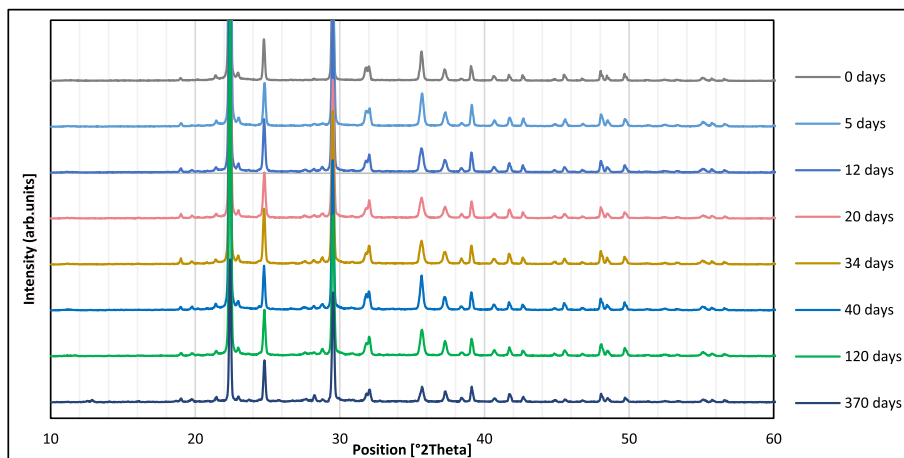
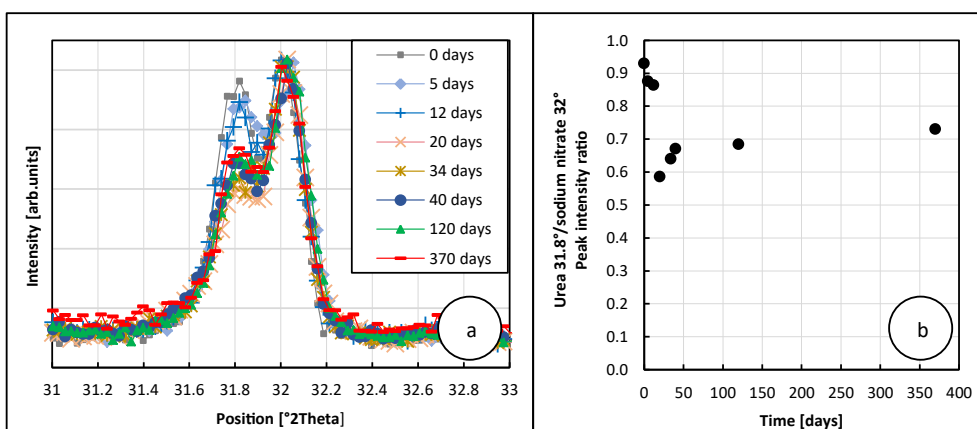**Fig. 12.** Evolution of the diffraction patterns of the samples tested for different times at 100 °C.

Fig. 13. a) Evolution of two characteristic peaks: urea (left peak) and sodium nitrate (right peak). b) Ratio of the intensity reached by the urea peak to the sodium nitrate peak of the samples analyzed.

sample tested for 20 days, after which the ratio reaches a stable intensity ratio. A similar proportionality change is also observed in the peaks placed at 2Theta positions 35.6° (corresponding to urea) and 39.2° (corresponding to sodium nitrate).

Although no quantitative conclusion can be drawn from the peak proportionality analysis, it points towards a significant degradation of the urea at the beginning, followed by a stabilization (under the operating conditions used).

The shape of the diffraction patterns also provides additional noteworthy observations. The baseline geometry of most of the degraded samples deviates to some extent from the pattern obtained in the non-degraded samples. This can be seen in Fig. 14, where the baseline of the signal corresponding to the degraded samples has a mild bell shape. From this change, it can be inferred that the samples exposed at 100 °C for a certain time have lower crystallinity than the fresh samples. This can indicate that part of the degradation products could be amorphous (no information can be extracted from the amorphous part by XRD).

3.5. Fourier-transform infrared spectroscopy (FTIR)

The FTIR analysis of the selected samples allowed us to determine the infrared spectra of the U-SN eutectic mixture samples exposed to 100 °C for different times. All the spectra resulted in a superposition of the original urea and sodium nitrate compounds, as depicted in Fig. 15.

None of the obtained spectra presented IR bands different from those present in urea and sodium nitrate, and as a result no other compounds could be identified. This confirms that urea and sodium nitrate make up
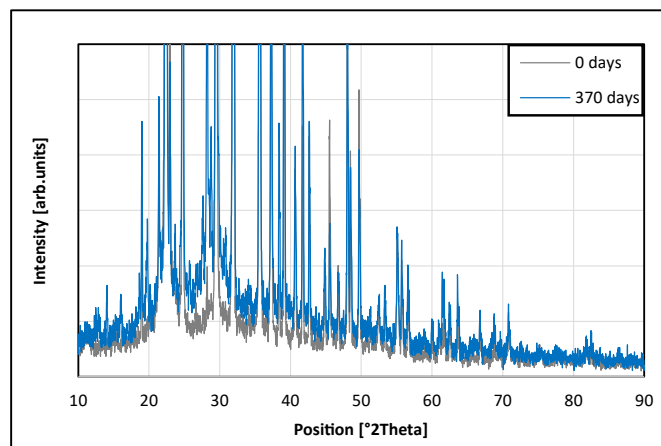

Fig. 14. Baselines of diffraction patterns for a non-degraded sample and one sample tested for 370 days at 100 °C.

the largest percentage of the samples, but it does not exclude the presence of other compounds in low proportions: their spectrum could have been hidden by the higher intensity of the principal compounds. A more exhaustive assessment could have been performed by a Beer-Lambert treatment, but it would not provide greater sensitivity than the HPLC and XRD results. Thus, further FTIR analysis was discarded.
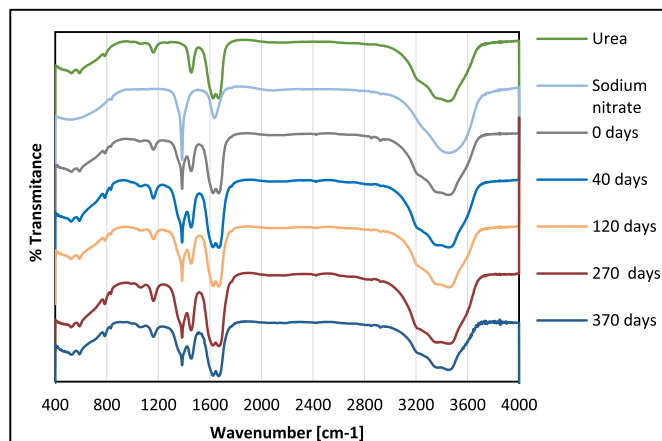
Fig. 15. FTIR spectra corresponding to pure urea, pure sodium nitrate, and the samples tested for 0, 40, 120, 270 and 370 days at 100 °C.

4. Discussion

While the main results obtained by different analytical techniques were presented in Section 3, a holistic discussion of the obtained information is presented here, in order to reach a useful understanding of the processes taking place.

While the XRD and FTIR results were useful to confirm that urea and sodium nitrate are the main constituents of all the samples submitted to thermal treatment, they were not suitable to quantify the presence of minor by-products. Thus, the discussion here focuses on the HPLC and DSC results.

4.1. Implications of the samples' mass-loss on the thermal degradation pathway
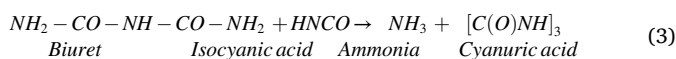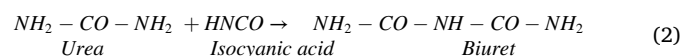
The first noteworthy aspect is related to the mass variation of the samples under thermal treatment. Although the DSC crucibles were supposed to be gas-tight under the experimental conditions used, a clear mass-loss was observed for most of the samples when they were weighed after being removed from the heating cabinet.

Fig. 16 compares the values of melting enthalpy (DSC) with the urea loss measured by HLPC (Fig. 16-a) and with the total mass-loss determined by weighing samples (Fig. 16-b).

It is noticeable that the urea loss measured by HPLC did not follow a chronological trend. This apparently incongruent behavior could be explained by the closing procedure of the crucibles, which was performed by a manually manipulated sealing press. Slight differences in the exerted pressure or in the position of the O-rings could have

rendered different tightness levels. In any case, this unwanted lack of tightness led us to conclude that the melting enthalpy is controlled by the urea loss (Fig. 16 a), and this loss was not directly related with the time that the samples were exposed to high temperature.

Fig. 16 b) shows that the latent enthalpy loss increases with mass-loss in a first stage, and afterwards stabilizes after 120 days, regardless of the increasing mass-loss in this second stage. Thus, the total mass-loss does not directly influence the melting enthalpy loss in all the testing times as urea loss does, which indicates that there are more than one process taking place. For a deeper understanding of this effect, the main degradation pathway of urea has to be analyzed. According to the literature, the most widely accepted thermal decomposition process comprises the following reactions [14–23]:

$$\underset{Urea}{NH_2 - CO - NH_2} \overset{\Delta}{\to} \underset{Ammonia}{NH_3} + \underset{Isocyanic\ acid}{HNCO} \tag{1}$$

$$\underset{Urea}{NH_2 - CO - NH_2} + \underset{Isocyanic\ acid}{HNCO} \to \underset{Biuret}{NH_2 - CO - NH - CO - NH_2} \tag{2}$$

$$\underset{Biuret}{NH_2 - CO - NH - CO - NH_2} + \underset{Isocyanic\ acid}{HNCO} \to \underset{Ammonia}{NH_3} + \underset{Cyanuric\ acid}{[C(O)NH]_3} \tag{3}$$

Based on the reaction pathway, it was concluded that the total mass-loss observed in the crucibles corresponds to the leaking of gaseous products, specifically ammonia and isocyanic acid.

To complete the results shown in Fig. 16, the urea loss was analyzed together with the evolution of biuret and cyanuric acid as a function of the samples' mass-loss. These are shown in Fig. 17. Two stages can be distinguished: for samples showing a total mass-loss below 0.5%, the urea decreases linearly with mass-loss while the biuret increases. For mass-loss values above 0.5 %, urea content remains almost constant, while the biuret decreases as the cyanuric acid increases.

In stage 1, both the decrease in urea and the increase in biuret vary almost linearly with the total mass-loss. As shown in equation (1), urea initially decomposes into gaseous ammonia and isocyanic acid, which is a highly reactive compound that reacts immediately with the urea to form biuret (equation (2)). In these steps, there is no formation of cyanuric acid. It can be concluded that the mass-loss in stage 1 corresponds to the production of volatile ammonia and isocyanic acid. Due to this leakage, the reaction moves towards further production of these gases, promoting further degradation of the urea.

In stage 2, the mass-loss is almost independent of the urea loss. As the mass-loss increases, the proportion of biuret reduces and the proportion of cyanuric acid increases. A plausible hypothesis is that, when the biuret content reaches a certain value, the reaction represented in equation (3) takes place, competing with the reaction in equation (2). Therefore, isocyanic acid combines with biuret to produce cyanuric acid and more ammonia gas.
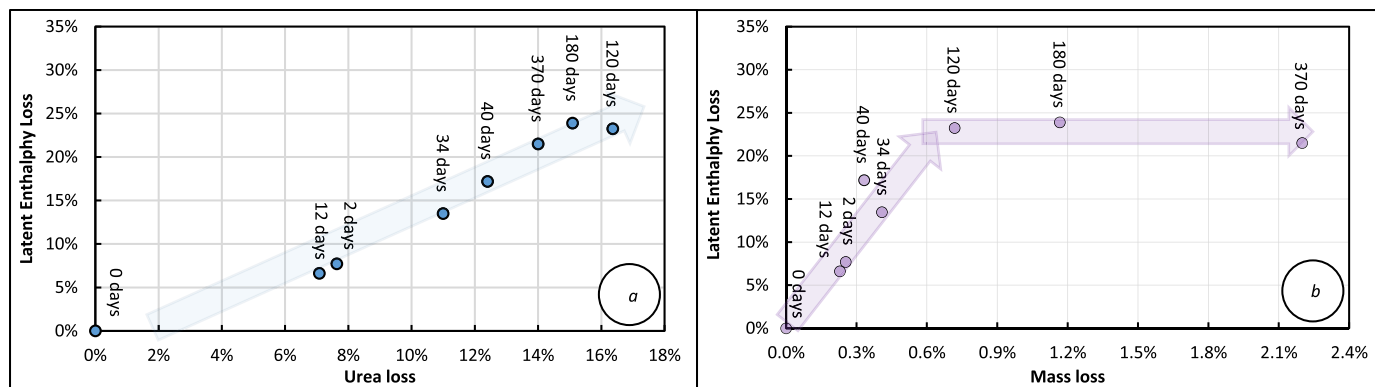

Fig. 16. a) Melting latent enthalpy loss measured by DSC vs.urea loss measured by HPLC; b) Melting latent enthalpy loss measured by DSC vs. mass loss measured using a precision laboratory scale.
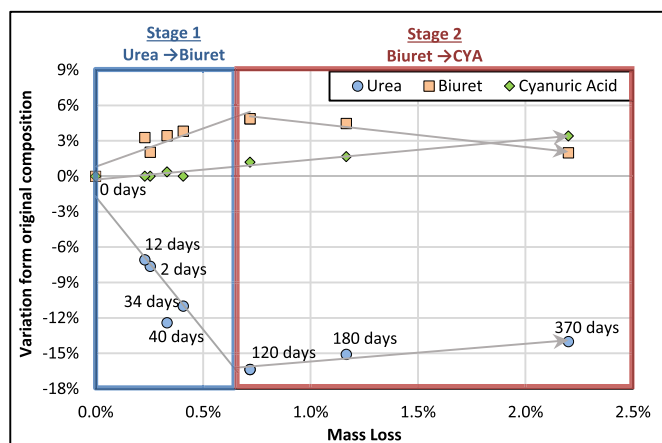
Fig. 17. Evolution of the composition (HPLC) versus total mass loss measured by weight difference before and after the testing period finished. The urea loss, biuret gain and cyanuric acid gain have been calculated as a percentage with respect to the theoretical urea mass contained in the samples if they were non-degraded.

In this situation, a potentially solid product is formed (cyanuric acid). In general, heterogeneous reactions where solid products are obtained are significantly slower than reactions that evolve into gaseous products, because the solid formation step controls the overall kinetics of the process. As a result, once the proportion of biuret in the mixture is sufficiently high, the urea degradation rate dramatically slows down. This is in accordance with the conclusion of Bernhard et al. [14] for reaction rates at 100 °C: the reaction rate of biuret formation (equation (2)) is higher than the reaction rate of cyanuric acid (equation (3)).

4.2. Relation between the DSC thermograms and the formation of thermal degradation products

The discussed urea loss and the formation of products other than urea and sodium nitrate changes the thermo-physical behavior of the material, as they modify the system phase-equilibrium. This can be observed on the DSC results shown in Figs. 9 and 10, where a decrease in the melting temperature (both onset and peak) can be noticed. For a deeper assessment, Fig. 18 shows the thermograms (second heating segment) of those samples, and the results obtained in the HPLC analysis. Each thermogram has been labeled with the percentage of biuret and cyanuric acid.
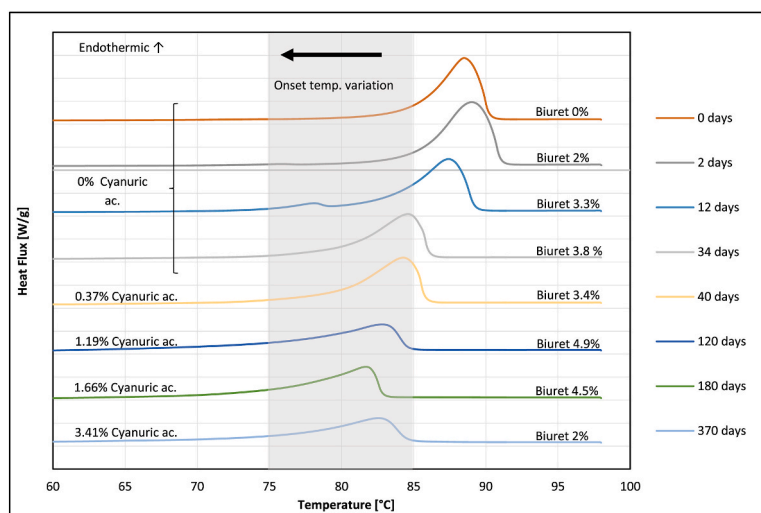
The geometry of the thermograms changes with increasing thermal exposure time. The melting onset-temperature decreases with increasing biuret percentage from 0% biuret (corresponding to 0 days) to 4.5% biuret (corresponding to 180 days). Afterwards, the biuret percentage decreases to 2% while the cyanuric acid percentage increases up to 3.4%, and the melting onset (and peak) temperature increases slightly. This case corresponds to the sample tested for 370 days. This behavior is an indication of the eutectic point modification (temperature and composition) since the system becomes ternary at the beginning (urea-biuret-sodium nitrate) and quaternary after long time exposure (urea-biuret-cyanuric acid-sodium nitrate). Results point towards a ternary eutectic mixture formed by urea-biuret and sodium nitrate with a eutectic melting temperature around 75 °C. Then, when the biuret percentage decreases and the cyanuric acid increases, the system is believed to become quaternary. This might lead to an increase in a liquidus temperature for the specific composition that was formed after 370 days. In any case, the observed increase is not significant.

This effect is accompanied with the decrease of the scattering of the crystallization temperature (observed in Fig. 7). This trend change can be taken as an additional sign of the transition from a ternary to a quaternary system, considering that the modification of the system characteristic transitions, can result in a change on the supercooling behavior. However, a deeper analysis of the crystallization behavior is out of the scope of this work.

In order to confirm this hypothesis, samples with different proportions of urea and biuret, containing 28.75 wt% sodium nitrate in all cases, were prepared and analyzed by DSC and XRD. The compositions analyzed were as follows: 3 wt% biuret - 68.25 wt% urea; 5 wt% biuret - 66.25 wt% urea; 7 wt% biuret - 64.25 wt% urea and 10 wt% biuret, 61.25 wt% urea. Fig. 19 shows the thermograms of these compositions, together with the thermogram of the urea and sodium nitrate eutectic composition.

Regarding the DSC study, the thermograms of most samples containing biuret show 2 peaks: the first has an onset temperature of 75 °C, and the second has different intensities and onset temperatures. The first peak is believed to correspond to the ternary eutectic signal and the second to the semi-solid range transition signal. The sample containing 10 wt% biuret shows one peak, but due to the irregular geometry with a posterior protuberance, it cannot be considered as the eutectic composition, with the protuberance corresponding to the semi-solid range transition, but very close to it.

The DSC analysis of the U-SN eutectic mixture samples degraded from 5 days up to 90 days showed (in most cases) DSC thermograms with two peaks. The starting temperature of the secondary peak coincides with the starting temperature of the hypothetical ternary biuret-urea-
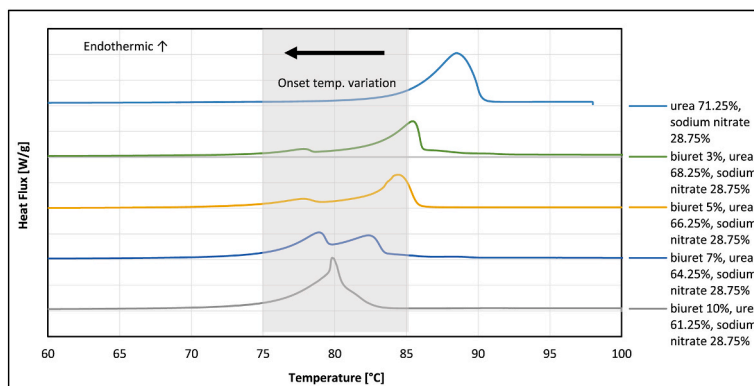

Fig. 18. Evolution of the DSC thermograms of selected samples, including the percentage of biuret and cyanuric acid in those samples (measured by HPLC).

Fig. 19. Thermograms of urea, biuret and sodium nitrate samples with different compositions of urea and biuret, prepared from the pure components to evaluate the phase transitions that occur with different compositions and the temperatures at which they occur.

sodium nitrate eutectic mixture, above mentioned. The DSC analysis of the samples degraded for longer periods, which contained a measurable proportion of cyanuric acid, show a single wide peak. Plausible explanations for the broadening of the peaks can be the superposition of two peaks or the existence of amorphous material in the samples. At present time, no published articles about these potential ternary or quaternary systems have been found in the scientific literature that could help to elucidate this uncertainty.

The XRD analysis of the urea-biuret-sodium nitrate samples, see Fig. 20, rendered the identification of sodium nitrate and urea crystalline phases, the lack of peaks corresponding to biuret or to biuret hydrate, and the presence of several extra peaks which do not belong to any of these compounds. Several of these match with a urea-biuret co-crystalline compound (ratio 1:1) in the PDF database (card #47–1948 corresponding with the compound (NH2)2CO_(NH2-CO)2NH)) [30,31]. However, several peaks remain non-identified, they did not match with any compound indexed in the database. These peaks indicate the presence of additional crystalline compounds formed in the system, which cannot be identified with the available state of the art. Their indexing and identification is out of the scope of the present work.

When comparing the diffraction patterns of the degraded U-SN eutectic mixture samples with those of the urea-biuret-sodium nitrate samples, the urea peaks and the sodium nitrate peaks match with each other, as well as some more few peaks. However, in both cases there are several peaks which do not match with each other, neither with any compound identified and indexed in the literature. Recently, Gross et al. [32] determined the formation of a co-crystalline compound composed

of biuret and cyanuric acid in a ratio of 1:1, when the biuret was heated at temperatures between 180 and 200 °C. The article includes the obtained XRD diffraction pattern and the IR spectrum. However, this compound is not yet indexed in the XRD databases even if the crystalline parameters are available and therefore, the correct identification of the peaks has not been possible. The XRD patterns of the degraded U-SN eutectic samples show several peaks that apparently match with some peaks of the XRD pattern shown in Ref. [32], corresponding to the biuret-cyanuric acid co-crystalline compound.

Summarizing, in the degraded samples there is evidence of the presence of co-crystalline compounds formed by urea and its by-products, although it is not possible to attain a conclusive identification of the phases due to their low proportion and to the lack of indexed information in the XRD databases.

4.3. Theoretical considerations on the chemical equilibrium during thermal degradation

The chemical reactions that take place in the urea and sodium nitrate system at a temperature around 100 °C are heterogeneous, i.e., gaseous, liquid and solid compounds form and interact. The production of gas compounds takes a major role in the equilibrium of the decomposition reaction and its kinetics, since it depends on the partial pressure of the gaseous products. If the PCM is contained in an effective gas-tight container, the degradation rate will be different from if the container leaks. Gas tightness is therefore an important parameter for the thermal stability of the U-SN eutectic mixture. The loss of the gaseous products
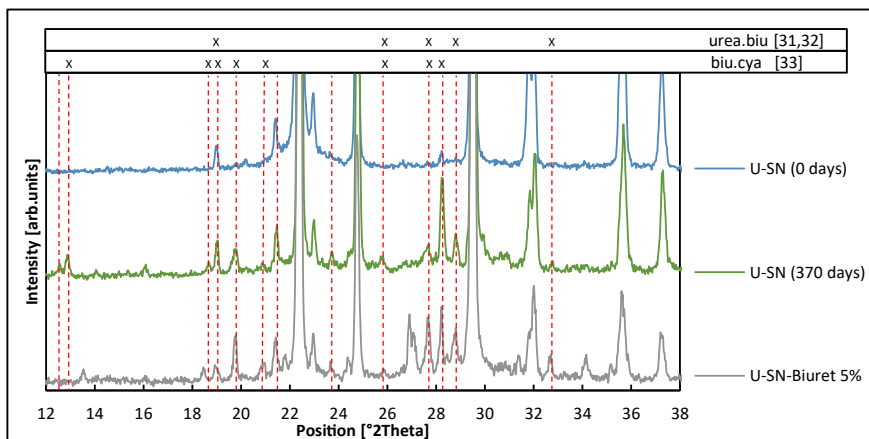

Fig. 20. Diffraction patterns of U-SN eutectic samples (non-degraded: 0 days, and degraded: tested for 370 days) and a sample containing 5 wt% biuret - 66.25 wt% urea - 28.75 wt% sodium nitrate (label: U-SN - Biuret 5%). The dashed lines correspond to the peak positions that do not match with urea and sodium nitrate diffraction patterns; the marks on the top indicate which positions may match with urea-biuret or biuret-cyanuric acid co-crystalline compounds.

causes the reaction to be displaced towards the formation of more products, promoting the degradation of the reagent, i.e., urea. If the material is placed in a tight container the degradation process will proceed until thermodynamic equilibrium is reached.

Therefore, under this assumption, the lifespan of the U-SN eutectic mixture as a PCM could be controlled to a large extent by the use of a gas-tight system, where the reaction evolution stops when the equilibrium pressure of the gaseous products is reached. However, the DSC crucibles that were used as gas-tight containers for PCM underwent small variations in mass over time. The mass variation after one year at a temperature above the melting temperature of the mixture did not exceed 2.2% of the initial mass. The mass-loss corresponds to a disturbance of the equilibrium conditions, which leads to further degradation of the urea. In this case, although the mass variation is small, the degradation produced has a great influence on the storage capacity of the system. This leads to two important observations: on the one hand, when the practical use of the material as a PCM is considered, tightness will be crucial. On the other hand, to study the long term behavior of PCMs, it is very important to take into consideration some experimental parameters that are commonly not taken into account, but which can have a great influence on the degradation and the thermal behavior of the systems. In this sense, the mass-loss is highlighted.

The production of gas-tight thermal storage devices can make a big difference to the behavior and lifetime of the PCM under operating conditions. Therefore, the proper design of LHTES devices to operate with the U-SN eutectic mixture as PCM should be gas-tight, made of a material that does not react with ammonia (discarded copper alloys), and designed to withstand an internal pressure greater than the equilibrium pressure (of the urea degradation process) without deformation or fracture. The determination of the system's equilibrium pressure is one of the mandatory steps for the proper design of such an LHTES device.

4.4. Implications of the thermal degradation on the behavior of the mixture as a PCM

To conclude, the implications of the observed degradation on the behavior of the mixture for thermal energy storage are herein discussed.

The obtained experimental DSC results could be considered as a reference for an operation of one year, under a maximum temperature of 100 °C. If this were the case, the obtained thermal properties would be suitable for the use of the mixture as a PCM for the intended application (DHW and heating). The finally achieved melting temperature (around 75 °C) remained within the application temperature range (60–95 °C). Regarding the energy storage density, the non-degraded U-SN eutectic mixture energy storage density is 245 kJ/dm^3 [2] and, after 370 days at 100 °C, would render a good latent energy storage density of 177.5 kJ/dm^3, a value within the range offered by typical paraffins (90–200 kJ/dm^3) [33].

Nevertheless, according to the previous discussion, the decrease in the thermal properties reaches a stabilization after the initial pronounced reduction, which is linked to the drastic slow-down of the urea-degradation, which presumably might be maintained permanently if adequate container conditions are met. Under these circumstances, the material could be used for longer periods of use. Further research should be performed to confirm this hypothesis.

5. Conclusions

A long-term study of the thermal stability and reliability of a PCM consisting of a eutectic mixture of urea and sodium nitrate was performed. The methodology consisted in keeping the molten samples at 100 °C for different periods of time, up to one year. Samples were analyzed by different techniques. The results revealed that the melting temperature and latent enthalpy values dropped by 10% and 24%, respectively, in the first 120 days and remained stable for up to one year.

The cause of the variation in the PCM thermal-properties is the decomposition of urea to produce other compounds. Biuret and cyanuric acid were identified in the degraded samples, which is consistent with the mechanisms of urea thermal decomposition proposed in the literature. It was determined preliminarily that biuret, urea and sodium nitrate form a ternary eutectic system with a eutectic temperature of around 75 °C. A full study of the ternary and/or quaternary systems formed by urea, sodium nitrate and the urea by-products would help to determine the characteristics of the potential mixtures formed during the degradation of the studied PCM.

Furthermore, the formation of these products is related to the mass-loss, which had an enormous relevance in the degradation of the materials. These findings highlight the importance of having a strict control of the handling and experimental parameters. Water uptake and, most importantly, mass-loss are parameters not usually taken into account for long-term degradation studies of PCMs. However, they can greatly influence the obtained results.

Based on the experiments, it was deduced that, if a gas-tight device is used, the eutectic mixture of urea and sodium nitrate can reach equilibrium and, consequently, the degradation process might be stopped. This could help to increase the lifespan of the mixture as a PCM. Further studies should effectively determine the equilibrium pressure of the system, which will serve to evaluate the feasibility of producing a cost-effective closed system compatible with the PCM and the byproducts.

Finally, the methodology proposed to study long-term degradation is thought to be adequate for PCM characterization, going a step further than the traditionally used accelerated cycling. In addition, it isolates the degradation process of the material by avoiding the influence of other phenomena related to crystallization, such as phase segregation, supercooling, polymorphism, etc. The analysis covers both thermal and compositional approaches so as to get a better understanding of the degradation mechanism, as well as potential cause and effect. In the study case, this allowed us to propose potential solutions to avoid the degradation of the material.

CRediT authorship contribution statement

Laura Quant: Investigation, Methodology, Validation, Writing – original draft. **Gonzalo Diarce:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Lourdes Bouzas:** Investigation. **Jean-Pierre Bédécarrats:** Supervision, Writing – review & editing. **Ana García-Romero:** Supervision, Funding acquisition, Project administration, Writing – review & editing.

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.

References

[1] H. Mehling, L.F. Cabeza, Heat and Cold Storage with PCM, 2008.

[2] G. Diarce, E. Corro Martínez, L. Quant, Á. Campos-Celador, A. García-Romero, The sodium nitrate-urea eutectic binary mixture as a phase change material for medium temperature thermal energy storage. Part I: determination of the phase diagram and main thermal properties, Sol. Energy Mater. Sol. Cells (2016) 1–11.

[3] G. Diarce, E. Corro Martínez, Á. Campos-Celador, A. García-Romero, J.M. Sala, The sodium nitrate-urea eutectic binary mixture as a phase change material for medium temperature thermal energy storage. Part II: accelerated thermal cycling test and water uptake behavior of the material, Sol. Energy Mater. Sol. Cells (2016) 1–8.

[4] J.-H. Li, G.-E. Zhang, J.-Y. Wang, Investigation of a eutectic mixture of sodium acetate trihydrate and urea as latent heat storage, Sol. Energy 47 (1991) 443–445.

[5] J. Lizana, R. Chacartegui, A. Barrios-padura, J.M. Valverde, C. Ortiz, Identification of Best Available Thermal Energy Storage Compounds for Low-To-Moderate Temperature Storage Applications in Buildings, vol. 68, 2018, p. 331.

[6] N.A. Pusci, M. Dezelie, Das Gleichgewicht in bin iren Systemen mit Erythrit als Komponente, 1932.

[7] L.F. Cabeza, a. Castell, C. Barreneche, a. de Gracia, a.I. Fernández, Materials used as PCM in thermal energy storage in buildings: a review, Renew. Sustain. Energy Rev. 15 (3) (Apr. 2011) 1675–1695.

[8] M. Gambino, J.P. Bros, 'Capacite calorifique de l'uree et de quelques melanges eutectiques a base d'uree entre 30 et 140ºC', Thermochim. Acta 127 (1988) 223–236.

[9] M. Kamimoto, R. Sakamoto, Y. Takahashi, K. Kanari, T. Ozawa, Investigation of latent heat-thermal energy storage materials. II. Thermoanalytical evaluation of urea, Thermochim. Acta 74 (1–3) (1984) 281–290.

[10] A. Sharma, S.D. Sharma, D. Buddhi, R.L. Sawhney, Thermal Cycle Test of Urea for Latent Heat Storage Applications vol. 468, 2000, pp. 465–468, 2001.

[11] C. Villada, A. Bonk, T. Bauer, F. Bolívar, High-temperature stability of nitrate /nitrite molten salt mixtures under di ff erent atmospheres, Appl. Energy 226 (2018) 107–115.

[12] W.M. Jacobs, et al., The thermal decomposition of sodium nitrate, Inorf. Phys. Theor. (1959) 1265–1268.

[13] T. Bauer, D. Laing, U. Kröner, R. Tamme, Sodium nitrate for high temperature latent heat storage, in: The 11th International Conference on Thermal Energy Storage – Effstock 14-17 June 2009 in Stockholm, Sweden, 2009, pp. 1–8.

[14] A.M. Bernhard, D. Peitz, M. Elsener, A. Wokaun, O. Kröcher, Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO 2, Appl. Catal. B Environ. 115 (116) (2012) 129–137.

[15] S. Sebelius, T.T. Le, L.J. Pettersson, H. Lind, 'Identification of urea decomposition from an SCR perspective ; A combination of experimental work and molecular modeling', Chem. Eng. J. 231 (2013) 220–226.

[16] A. Lundström, B. Andersson, L. Olsson, Urea thermolysis studied under flow reactor conditions using DSC and FT-IR, Chem. Eng. J. 150 (2–3) (2009) 544–550.

[17] D. Wang, N. Dong, S. Hui, Y. Niu, Analysis of urea pyrolysis products in 132.5-190 °C, Energy Procedia 158 (2019) 2170–2175.

[18] H.L. Fang, H.F.M. DaCosta, Urea thermolysis and NOx reduction with and without, SCR catalysts', *Appl. Catal. B Environ.* 46 (1) (2003) 17–34.

[19] M. Koebel, M. Elsener, Determination of Urea and its Thermal Decomposition Products by High-Performance Liquid Chromatography vol. 689, 1995, pp. 164–169.

[20] P.M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, J. Brauer, Thermal decomposition (pyrolysis) of urea in an open reaction vessel, Thermochim. Acta 424 (1–2) (2004) 131–142.

[21] S. Tischer, M. Börnhorst, J. Amsler, G. Schoch, O. Deutschmann, Thermodynamics and reaction mechanism of urea decomposition, Phys. Chem. Chem. Phys. 21 (30) (2019) 16785–16797.

[22] S. Désilets, et al., Degradation mechanism and thermal stability of urea nitrate below the melting point, Thermochim. Acta 521 (2011) 176–183.

[23] S. Désilets, et al., Analyses of the thermal decomposition of urea nitrate at high temperature, Thermochim. Acta 521 (2011) 59–65.

[24] S.H.C. IEA, Solar Heating & Cooling Programme IEA Task 58, Material & Components for Thermal Energy Storage', 2019. http://task58.iea-shc.org /subtasks.

[25] M.K. Rathod, J. Banerjee, Thermal stability of phase change materials used in latent heat energy storage systems A review, Renew. Sustain. Energy Rev. 18 (2012) 246–258.

[26] C. Rathgeber, et al., Experimental devices to investigate the long-term stability of phase change materials under application conditions, Appl. Sci. 10 (22) (2020) 1–30.

[27] Compact Karl fischer moisture meter KF-31. https://www.mccat.co.jp/global/ins trument/karl-fischer/entry-171.html.

[28] H. Zahir, S.A. Mohamed, R. Saidur, F.A. Al-sulaiman, Supercooling of phase-change materials and the techniques used to mitigate the phenomenon, Appl. Energy 240 (July 2018) 793–817, 2019.

[29] A. García-Romero, G. Diarce, J. Ibarretxe, A. Urresti, J.M. Sala, 'Influence of the experimental conditions on the subcooling of Glauber's salt when used as PCM', Sol. Energy Mater. Sol. Cells 102 (2012) 189–195.

[30] A.L. Voskov, T.S. Babkina, A.V. Kuznetsov, I.A. Uspenskaya, Phase equilibria in the urea-biuret-water system, J. Chem. Eng. Data 57 (11) (2012) 3225–3232.

[31] T.S. Babkina, A.V. Kuznetsov, Phase equilibria in binary subsystems of urea-biuret-water system, J. Therm. Anal. Calorim. 101 (1) (2010) 33–40.

[32] P. Gross, H.A. Hçppe, 'Biuret — A Crucial Reaction Intermediate for Understanding Urea Pyrolysis to Form Carbon Nitrides : Crystal-Structure Elucidation and in Situ Diffractometric , Vibrational and Thermal Characterisation', 2020, pp. 14366–14376.

[33] M.M. Kenisarin, Thermophysical properties of some organic phase change materials for latent heat storage, A review', *Sol. Energy* 107 (2014) 553–575.