

# Xylitol Used As Phase Change Material: Nucleation Mechanisms Of The Supercooling Rupture By Stirring

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**Abstract**—Owing to its high energy density, Xylitol is a very promising Phase Change Material (PCM) for low temperature applications ( $< 100^{\circ}\text{C}$ ). However, it presents a high and persistent supercooling that inhibits the latent heat restitution during thermal discharges. Bubbling in the supercooled PCM is known as an efficient way to trigger Xylitol crystallization. This paper proposes an experimental investigation leading to a new description of the nucleation mechanisms behind this triggering technique based on secondary nucleation. Adding a seeding step to the crystallization process is also proposed to increase the efficiency and reproducibility of the heat restitution.

**Keywords**—Thermal energy storage, Phase Change Material, Sugar Alcohols, Crystallization activation, Bubbling, Nucleation

## I. INTRODUCTION

The European Commission identified the use of district heating networks as an efficient way to integrate renewable energies or wasted heat and to reduce  $\text{CO}_2$  emissions. Heat storage is a key component for next generation of urban heating networks to deal with the shift between intermittent production and heat demand. Latent Heat Thermal Energy Storage (LHTES) systems are particularly suitable for decentralized heat storage applications directly in the building substations of a district heating network [1], [2]. To be competitive with centralized sensible heat storage systems, the development of new Phase Change Materials (PCM) with high energy storage densities is necessary. The ideal PCM for such an application must have a melting temperature below  $100^{\circ}\text{C}$  and a high energy density ( $> 100 \text{ kWh}\cdot\text{m}^{-3}$ ). It must also be cheap and match the requirements of the building's application (non-toxic, non-flammable and environmentally friendly). Sugar Alcohols (SA) were recently identified as promising PCMs for such applications [3], [4]. Among SAs, Xylitol has a particularly high potential: a melting temperature of  $93.5^{\circ}\text{C}$ , a latent heat of  $267 \text{ J/g}$  and a total energy density

much higher than sensible storage in water (near  $120 \text{ kWh}\cdot\text{m}^{-3}$  considering a temperature range from  $30^{\circ}\text{C}$  to  $104^{\circ}\text{C}$ ) [3]. Moreover, it is currently used as a sweetener by the agribusiness industry, which makes it cheap and edible so non-toxic. Nevertheless, two main issues are still to be solved before an industrial application: its long term chemical stability that has not been studied already and its high and persistent supercooling [4]. This work focuses on the supercooling challenge.

Xylitol supercooling exhibits a very low primary nucleation rate, making it uncrystallizable only by cooling [5]. Making that attribute an advantage, Duquesne et al. [6] proposed to use Xylitol for long term LHTES. Moreover, because of its high viscosity, Xylitol has a very low crystal growth rate with a maximum rate of roughly  $3.5 \mu\text{m/s}$  at  $62^{\circ}\text{C}$  [7], which reduces drastically the heat restitution speed. For this reason, a LHTES system using Xylitol as PCM must include a nucleation triggering technique that creates many nuclei. This way, the increased total growing surface offsets the low Xylitol crystal growth rate and reduces the overall discharging time. Different techniques have already been tested to trigger Xylitol crystallization; local cooling failed to initiate crystallization [4], seeding and ultrasounds had a very localized effect and could not create enough nuclei [8]. The use of additives did not accelerate the crystal growth enough to get reasonable discharging times [9]. Mechanical agitation would be too intrusive and too difficult to implement in an industrial system. Duquesne et al. [6] identified agitation by bubbling as an interesting solution to trigger the nucleation and to initiate the heat restitution. By bubbling, they managed to form many nuclei in a few minutes in a beaker of supercooled Xylitol at  $75^{\circ}\text{C}$ . Their current hypothesis is that small bubbles in suspension act as nucleation sites for a primary heterogeneous nucleation. Then, the agitation disperses these new nuclei in the stirred volume of PCM.

Moreover, as Beaupere et al. [10] explained, the primary heterogeneous nucleation rate could be influenced by the agitation. On the other hand, Delgado et al. [11] studied shearing and seeding in supercooled Xylitol to trigger its crystallization, emphasizing on the effect of secondary nucleation. The mechanisms behind nucleation in stirred Xylitol seem to be complex and not fully understood. In this paper, these mechanisms were experimentally explored for a mechanical and bubbling agitation.

## II. THEORY OF NUCLEATION

In this section, elements of nucleation theory in supercooled melts are briefly introduced in order to discuss the crystallization mechanisms studied in this work. Then previous literature working on Xylitol crystallization is assessed in its light.

### A. Nucleation mechanisms and their kinetics

Supercooling is a metastable state in which a material can exist as a liquid below its melting temperature. The nucleation theory describes the mechanisms behind the formation of the first small crystals called nuclei that allow to switch from this metastable state to a more stable one, the crystalline form. It is a problem of kinetics represented by the nucleation rate, which corresponds to the number of nuclei appearing per unit of volume and time in the supercooled melt.

These nuclei can come from different mechanisms. Fig. 1 outlines the three main ones. First, the distinction is made between primary and secondary nucleation. Nuclei formed by primary nucleation directly come from the liquid phase. The molecules in the liquid phase reorganize themselves into a crystalline structure. Supercooling is the result of a low primary nucleation rate: for highly viscous melts for example, the low diffusivity of the molecules in the liquid phase prevents them from reorganizing. A triggering technique would then be required to overcome the energy barrier of the metastable state.

A distinction is made between homogeneous and heterogeneous primary nucleation. Homogeneous nucleation is defined by the appearance of nuclei in the bulk of the liquid whereas heterogeneous nucleation occurs on foreign particles or surfaces that facilitate crystallization by reducing the energy barrier to cross for nuclei formation. The addition of nucleation sites may increase the heterogeneous nucleation rate.

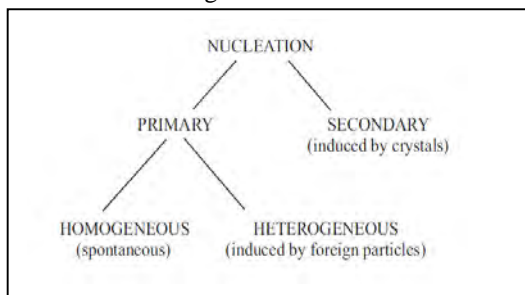


Fig. 1. The different nucleation mechanisms

On the other hand, secondary nucleation can only happen in stirred melts and in the presence of first parental crystals. Shocks between crystals, the stirring device or the tank walls can result in the formation of new nuclei. Shearing can also directly rip off crystalline particles from the parental crystals. All these mechanisms need the presence of the crystalline phase, which means that secondary nucleation only allows the creation of more nuclei but cannot break the metastable state by itself. In industrial crystallizations, seeding is often used to start the secondary nucleation. A small amount of the crystalline form of the same product is introduced in the stirred tank and these seeds act as the required first parental crystals.

### B. Nucleation in stirred Xylitol

According to the different mechanisms detailed above, the first nuclei needed for the supercooling rupture can only come from primary nucleation or seeding. Then, either primary or secondary nucleation (or both) can explain the massive formation of nuclei that triggers the heat restitution.

Without stirring, it has been shown that Xylitol can stay as a liquid at any supercooling degree [4], [5], which means that pure Xylitol has a very low primary nucleation rate. In the literature, Duquesne et al. [6] triggered Xylitol nucleation by stirring without seeding. They proposed the hypothesis of an intense primary heterogeneous nucleation at the surface of small bubbles in suspension in the stirred Xylitol. They did not study the possibility of secondary nucleation. However, good nucleation sites are often chosen for their crystalline structure similar to the main product, and the fact that small bubbles are so efficient would need more justification. They also did not explore the possibility that agitation could increase the primary nucleation rate. So, is it really the addition of nucleation sites (the bubbles) or the agitation itself that triggers the nucleation?

The work of Delgado et al. [11] studied secondary nucleation, by shearing in seeded samples of supercooled Xylitol. They show that a massive formation of nuclei is possible by secondary nucleation. Since they used seeding to start their crystallization process, they do not conclude anything on the feasibility of triggering primary nucleation in Xylitol by stirring.

The present work explores which nucleation mechanism could be efficiently used to trigger crystallization of Xylitol, with or without seeding.

## III. PRIMARY NUCLEATION IN STIRRED XYLITOL

The feasibility of triggering primary nucleation by stirring is first studied in this section.

**A. Triggering Xylitol crystallization by shearing**

The first studied system, shown in Fig. 2, is a plate-plate rheometer MCR300 with 2 mL of supercooled Xylitol maintained at 50°C by a Peltier element. Xylitol purchased from Danisco (purity 98.5%) was composed of aggregates of an equivalent diameter D50 of 180 μm. The shear rate was fixed at 50 s<sup>-1</sup>. The viscosity of the Xylitol sample was measured to detect the nucleation by an increase in viscosity. This experiment was based on the previous work of Delgado et al. [11], but without seeding the Xylitol sample. The sample was first heated for three hours at 105°C to ensure a complete melting. To protect the sample from unintentional seeding, a tap was placed upon the sample and the rheometer was placed in a clean room where crystalline Xylitol had not been handled before. The experimental trial started with a linear cooling ramp to reach 50°C in one hour with continuous shearing. Then, the sample was sheared at 50°C until nucleation started. The shearing stopped as soon as an increase in viscosity was detected.

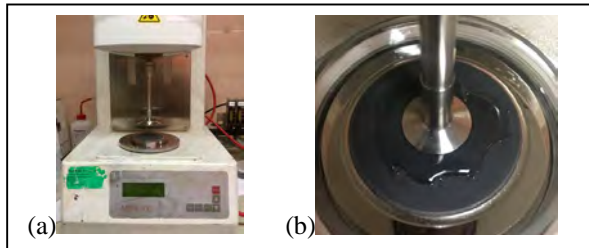


Fig. 2. Triggering Xylitol nucleation by shearing: (a) a plate-plate rheometer MCR300; (b) a 2 mL Xylitol sample sheared at 50 s<sup>-1</sup> with a PP25.

Fig. 3 presents a typical test result for the rheometer, plotting the target temperature of the sample and the measured viscosity. The Xylitol sample's viscosity first increases when the sample temperature decreases following Shao et al. [12] viscosity curves. Then the sample can be sheared indefinitely without succeeding in triggering nucleation. Fig. 3 only shows two hours of shearing to provide an overview of the cooling ramp but 48-hour trials were not successful either. Other shear rates (from 1 s<sup>-1</sup> to 500 s<sup>-1</sup>) and sample temperatures (from 30 to 90°C) were also tested, unsuccessfully. Shearing does not affect the Xylitol nucleation rate enough to trigger its crystallization in reasonable time scales. However, the lack of nucleation sites and the small sample size also contributed to make the crystallization difficult.

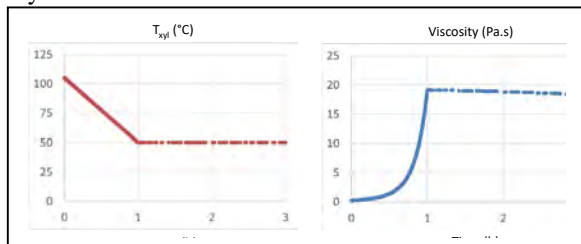


Fig. 3. Trial to initiate the Xylitol crystallization by shearing in a rheometer PP50 with a shear rate of 50 s<sup>-1</sup> and a distance plate-plate

$d = 1 \text{ mm}$ . On the left: sample temperature controlled by a Peletier element. On the right: measured sample viscosity

It can also be observed in Fig. 3 that the viscosity of Xylitol seems to slowly decrease with time for a constant sample temperature and shear rate. Shao et al. [12] showed that Xylitol is a non-Newtonian fluid for shear rates smaller than 1 s<sup>-1</sup>. The observed decrease in viscosity could be explained by a thixotropic behavior, which will not be discussed more in this work.

**B. Triggering Xylitol crystallization by stirring**

A second system includes a beaker with 20 mL of Xylitol and a magnetic stirrer (Fig. 4). The beaker was hermetically closed and placed in an oven at 105°C overnight to ensure a complete fusion. The next day the beaker was placed upon a magnetic agitation plate. The sample temperature was fixed to approximately 70°C using the electric heater of the agitation plate. The direct measurement of the sample temperature would be impossible because the beaker would have to be opened to introduce the thermocouple, leading to unintentional seeding. A first trial was therefore conducted only to set the heater to get 70°C in the stirred sample.

In the hermetically closed beaker, no crystallization occurred even after two weeks of stirring at 70°C. Not a single nucleus appeared in the stirred volume, which gives an order of magnitude for the nucleation rate in the stirred beaker:

$$J \ll 1/V \cdot \Delta t \sim 10^{-8} \text{ s}^{-1} \text{ cm}^{-3}$$

This beaker already involved many possible nucleation sites (impurities, small bubbles created by the agitation, surface roughness, etc). Neither the presence of these nucleation sites nor the agitation allowed to trigger primary nucleation.

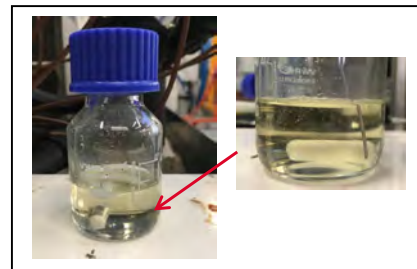


Fig. 4. Triggering nucleation by stirring: a hermetically closed beaker filled with 20 mL of Xylitol and a magnetic stirrer. After two weeks of stirring, a thermocouple measures the sample temperature: 70°C.

**C. Secondary nucleation and unintentional seeding**

If triggering primary nucleation by stirring seems impossible, a scenario based on secondary nucleation is still possible. However, such a scenario requires a seeding step.

Still with the previous small beaker and as soon as the hermetic tap is removed, nucleation started in a few seconds. This result matches with Duquesne et al. [6]

previous observations. However, without this hermetic tap, the main sample is not protected from unintentional seeding: a crystalline Xylitol dust can settle at the free surface and act as a parental crystal to trigger secondary nucleation, which is an intense mechanism, as shown by Delgado et al. [11].

To strengthen the hypothesis of an unintentional seeding, a beaker filled with supercooled Xylitol is simply placed in the lab. After a dozen hours, crystals indeed appear at the free surface of the Xylitol sample, as shown in the picture in Fig. 5. These crystals have to grow beyond a certain size to be visible, indicating that, in reality, they may have formed much earlier. Since Duquesne et al. [6] did not isolate their crystallizer from unintentional seeding and because triggering primary nucleation seems so hard, it is likely that the massive formation of nuclei they observed came from a secondary nucleation allowed by an unintentional seeding of their reactor.

In their work, Duquesne et al. [6] observed a small cavity at the center of the nuclei formed in their airlift reactor. Since the bubbles are unlikely to activate the primary nucleation, these holes could be explained by a volume retraction of the solid phase during crystallization. Another possibility is that crystalline particles ripped off by secondary nucleation could preferentially settle at the surface of the bubbles in suspension.



Fig. 5. Unintentional seeding at the free surface of a Xylitol sample kept in the lab atmosphere after 10 hours of supercooling.

#### D. Discussion on unintentional seeding and Xylitol

In his book *Crystallisation*, Mullin [13] dedicated pages 199 to 201 to the unintentional seeding problem: “unintentional seeding, also frequently encountered in both laboratory and industry, is an uncontrolled event which can often cause considerable frustration and trouble”. Atmospheric dust frequently contains particles of the crystalline product that has been handled in the laboratory. Moreover, as an illustration, Mullin precisely takes the example of Xylitol and its industrial production history. Xylitol, first prepared in 1891 was considered to be liquid until 1941 when a solid form melting at 61°C unexpectedly crystallized. Two years later, another form melting at 93.5°C appeared and completely replaced the first less stable polymorphic form. Nowadays, this crystalline form melting at 61°C has completely disappeared and any attempt to crystallize it leads to the more stable form. This case of

disappearing polymorph is also quoted by Dunitz and Bernstein [14].

This literature testimony gives new insights into the understanding of Xylitol crystallization and goes in favor of the impossibility to activate primary nucleation in reasonable time scales. In this literature testimony, Xylitol globally stayed liquid for 50 years because of its very low primary nucleation rate. So, it seems ambitious to trigger its primary nucleation simply by stirring. The first polymorphic form to appear was the less stable one because the energy barrier to overcome for its formation was probably lower than the one necessary to create the more stable form. This phenomenon is known as the Ostwald’s rule of stages. It means that it would be easier to trigger the primary nucleation of this less stable form than the current one. Nevertheless, both are unlikely; rather all Xylitol crystallizations are initiated by seeding (intentionally or not). As Dunitz and Bernstein [14] explain and because primary nucleation of Xylitol occurred at least once, it would necessarily be possible to trigger the primary nucleation of any Xylitol polymorph again. Nevertheless, it requires finding the right experimental conditions and waiting long enough.

Due to the low primary nucleation rate of Xylitol, a nucleation triggering strategy based on the use of nucleative agents has very small chances of being successful. Seeding, intentionally or not, is currently the only way to initiate Xylitol crystallization in reasonable times for a heat storage application.

The next section reproduces the experimental results of Duquesne et al. [6], triggering nucleation by bubbling in an airlift reactor, in light of this new description of the nucleation mechanisms.

#### IV. EXPERIMENTAL SET-UP

This section proposes an efficient triggering technique for Xylitol crystallization by stirring and seeding. Two double-walled crystallizers filled with stirred supercooled Xylitol are studied in this work: one with a mechanical agitation and the other with an agitation by bubbling. The comparison was made between thermal discharges with or without a seeding step for both types of agitation.

##### A. Airlift INOX crystallizer

The first studied crystallizer, shown in Fig. 6, is an airlift metallic cylindrical reactor with 400 mL of PCM. A gas injection of N<sub>2</sub> creates bubbles at the bottom of the reactor. The gas flow was controlled by a flow sensor and fixed at 1 L.min<sup>-1</sup>. The needle was slightly inclined to ensure the most reproducible agitation possible. To reduce unintentional seeding, a tap was placed at the top of the crystallizer. The double-walled vessel was connected to a thermal bath using silicone oil (SilOil M40) as transfer fluid to control the sample temperature. Two thermocouples measure the thermal oil inlet and outlet temperatures. Nine T-type 1mm

thermocouples were immersed into the PCM sample at different positions to check the homogeneity in temperature of the stirred Xylitol and to detect the start of the heat restitution by an increase in the sample temperature. This increase in temperature is the result of the growth of many newly formed nuclei.

**B. Mechanical agitation in a glass crystallizer**

A second double-walled crystallizer was also set up for comparison (Fig. 7). The agitation by bubbling was replaced with mechanical agitation by a propeller compatible with Xylitol’s viscosity at 70°C and a motor Heidolph RZR 2041 assuring a constant rotational speed fixed at 150 rpm. Moreover, the glass double-walled container allows to follow the crystallization visually. A tap was also placed at the top of the beaker to avoid unintentional seeding. The crystallizer was filled with 300 mL of PCM and a T-type thermocouple was plunged into the Xylitol to measure the sample’s temperature and to detect the nucleation. The double wall was connected to a thermal bath using the same silicone oil as in the previous crystallizer.

**C. Discharge protocol**

Two kinds of experimental tests were conducted in each crystallizer: with and without adding a seeding step to the discharge protocol. In all the tests performed, Xylitol was initially melted at 105°C overnight to ensure that the whole sample was liquid. Then, the sample was cooled down by setting the thermal bath to 70°C. It was also continuously stirred during the cooling ramp. For tests with the seeding step, 20 mg of the Danisco crystalline Xylitol powder were introduced in the supercooled melted sample when its temperature passed below 90°C. The seeds were introduced through a hole in the tap at the top of the crystallizer and were simply settled at the free surface of the main sample. The seeds could not melt because the crystallizer temperature was already lower than the Xylitol melting temperature (93.5°C). Nevertheless, they were not expected to initiate the heat restitution by themselves because the creation of many nuclei was still necessary to offset the Xylitol low crystal growth rate.

Fig. 8 presents the experimental setting of both crystallizers during discharge.

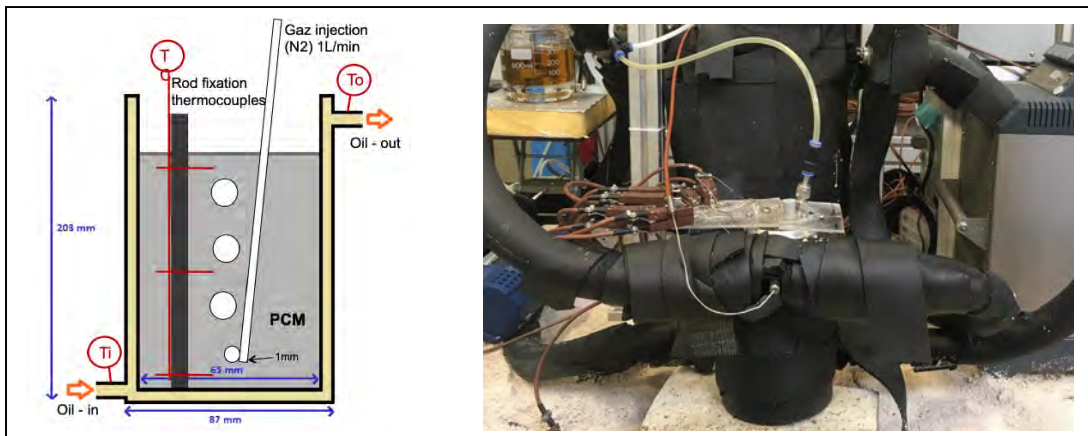


Fig. 6. Schematic view of the used airlift INOX double-walled crystallizer filled with 400 mL of Xylitol and picture of the whole thermally insulated experimental bench.



Fig. 7. The glass double-walled crystallizer filled with 300 mL of Xylitol mechanically stirred by a propeller and a motor rotating at 150 rpm.

	PCM volume	Thermal bath temperatures	Agitation
Airlift INOX crystallizer	400 mL	105°C to 70°C	By bubbling: 1 L/min Needle diameter: 1 mm
Glass crystallizer	300 mL	105 to 70°C	Propeller: 150 rpm Propeller diameter: 6 cm

Fig. 8. Experimental setting of the discharges for both crystallizers.

The measured sample temperature was used to calculate the induction time between the beginning of supercooling, when the sample passed below its melting temperature of 93.5°C, and the start of crystallization, detected by an increase in the sample temperature. This measured induction time is the sum of two factors: nucleation time, a delay in the formation

of nuclei in the stirred supercooled PCM, and growth time, necessary for these new nuclei to grow enough to initiate the heat restitution. The more intense the nucleation is the shorter will be this induction time. It was also used to compare the discharges with or without the seeding step. For a real heat storage system, it would be important to reduce this latency as much as possible, because it results in a delay in the heat restitution and a variation in the restituted temperature.

V. RESULTS

A. Monitoring temperature of the sample

The measured temperature of the Xylitol sample is presented in Fig. 9 for the mechanical agitation and Fig. 10 for the bubbling agitation. In Fig. 9, five discharges without seeding and three with the seeding step are plotted for the exact same experimental settings (a mechanical agitation of 150 rpm). For each trial, the corresponding measured induction time is also

represented. A cross symbolizes the seeding time of the three discharges with the seeding step.

Three pictures of the sample at different times are also added in Fig. 9 for one of the tests without the seeding step. The first picture represents the sample at  $t_0$  when the Xylitol is completely melted. The second one is taken at the beginning of heat restitution when the sample temperature starts to increase. In this picture, many nuclei can be observed in the reactor. The last picture represents the sample one minute later, during the heat restitution. The sample then looks like a growing solid.

For the five trials without seeding, the measured induction time varied from a few minutes to several hours, whereas the experimental conditions were the same. On the other hand, the induction time of the three trials with the seeding step were shorter and reproducible.

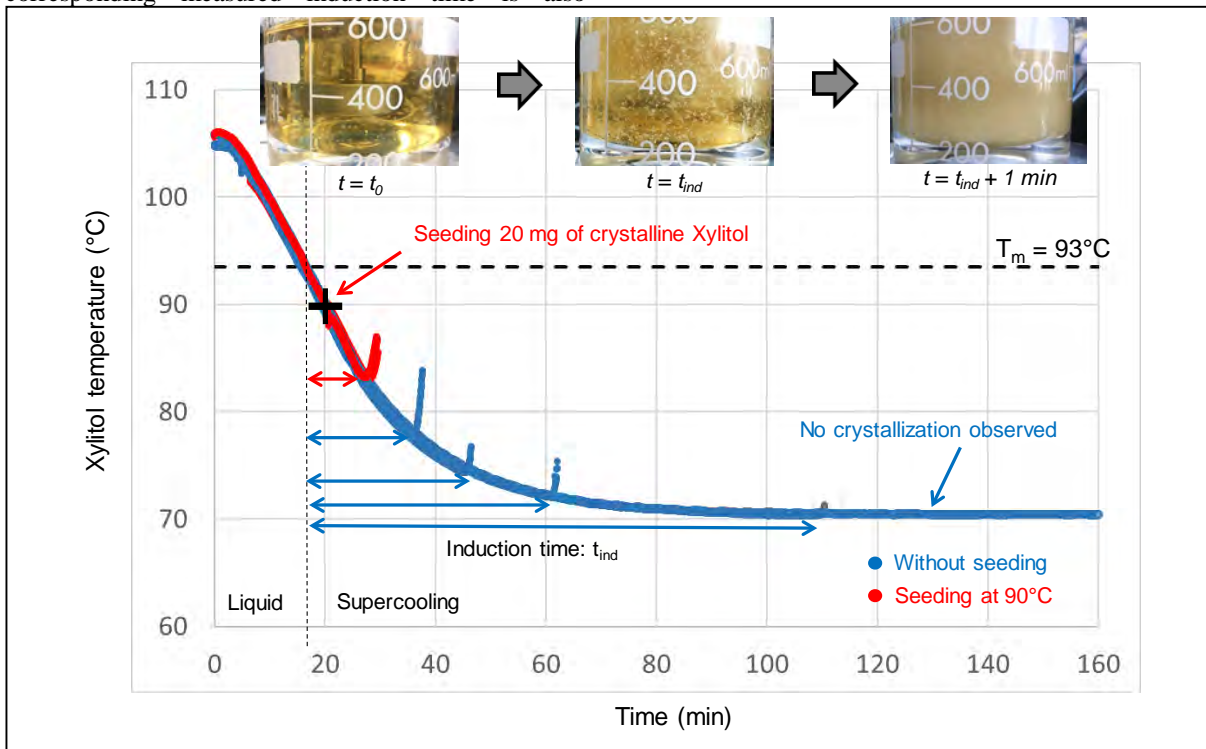


Fig. 9. Thermal discharges with or without seeding with a mechanical agitation. Rotational speed: 150 rpm. Temperature of thermal bath: 70°C.

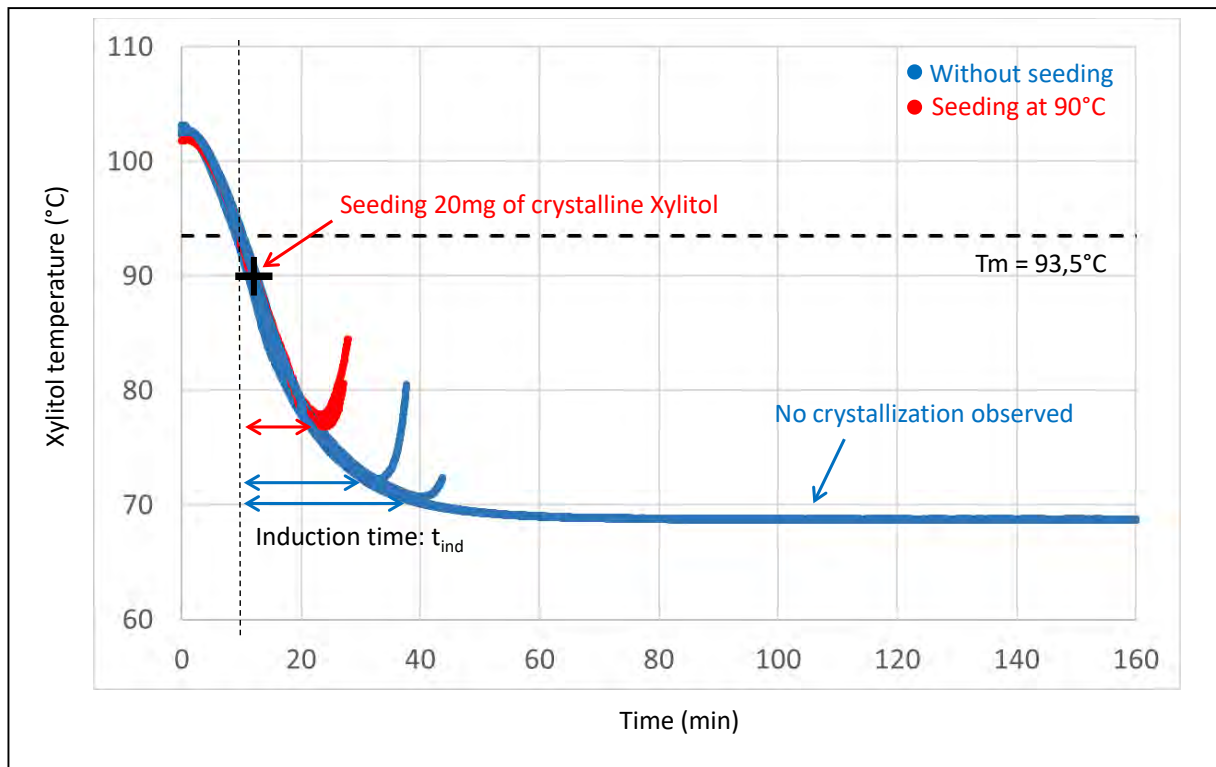


Fig. 10. Thermal discharges with or without seeding for a bubbling agitation. Gas flow: 1 L/min. Temperature of thermal bath: 70°C.

For the airlift reactor, six discharges without the seeding step and three with it are plotted in Fig. 10. Four trials among the six without seeding did not crystallize after two hours of bubbling. Again, adding this seeding step induced shorter and reproducible induction times. Fig. 11 presents all the measured induction times for both crystallizers with or without the seeding step.

Induction times (min)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6
Bubbling agitation	23	30	>150	>150	>150	>150
Bubbling + seeding	12	13	13			
Mechanical agitation	19	29	44	92	>150	
Mechanical agitation + seeding	10	11	11			

Fig. 11. Measured induction times (in minutes) in the two crystallizers with or without seeding.

### B. A lack of reproducibility without seeding

According to the obtained induction times, triggering Xylitol crystallization by stirring without seeding the reactor may be possible but this technique is clearly not reproducible and has a random aspect. When the crystallization starts, many nuclei are formed as shown in the second picture in Fig. 9. Even if the crystallizer was not seeded, these nuclei were surely formed by secondary nucleation as discussed earlier. The tap placed at the top of the crystallizers was not

sufficient to protect them from unintentional seeding, probably due to a Xylitol dust that settled at the free surface, as observed in Fig. 5.

The fact that more trials with no crystallization were observed for the airlift reactor than for the mechanical agitation could be explained by the gas flow. Nitrogen injected at the bottom of the bubbling crystallizer had to leave from the top of the reactor, creating a gas flow going out of the crystallizer that could have contributed to isolate the main sample from dust in the atmosphere. Both crystallizers were placed in the same lab.

It seems impossible to reproduce results from previous literature [6] and the reproducibility of the triggering method proposed by Duquesne et al. may be questioned. It would be interesting to conduct the same experiments at a pilot scale to check if the unintentional seeding event is more likely to occur in bigger systems.

### C. Triggering Xylitol crystallization by seeding and stirring

By adding a seeding step to the discharge protocol, the crystallization triggering was fast and reproducible for both crystallizers. For such tests, initialization of secondary nucleation did not depend on a random contact with dust, but rather started as soon as the seeds were introduced. Seeding and stirring appears to be a promising method to trigger Xylitol crystallization.

It is interesting to note that the heat restitution does not started immediately after seeding. As explained before, the seeds themselves were not sufficient to

trigger the crystallization because a massive formation of nuclei was still necessary. The latency between the seeding event and the start of heat restitution depends on two mechanisms, the secondary nucleation to create many nuclei and the growth of these nuclei to reconstitute enough heat to be detected. It seems impossible to determine which mechanism is kinetically limiting.

If seeding is crucial for both crystallizers to get fast and reproducible induction times, it is difficult to compare one crystallizer with the other. Even if the measured induction times were shorter for mechanical agitation, the cooling speed was higher in this crystallizer and the stirring fluid mechanics were completely different. Future work will focus on a parametric study of this secondary nucleation induction time.

#### CONCLUSION

Bubbling was already known as a low intrusive and promising way to trigger supercooled Xylitol crystallization but the nucleation mechanisms involved are particularly complex. In this paper, it has been shown that it is impossible to trigger Xylitol primary nucleation in reasonable time scales. Most of the nuclei formed in a bubbling crystallizer probably come from secondary nucleation. The increased total growth surface then allows to offset the low crystal growth rate of Xylitol and to initiate the heat restitution.

Without intentional seeding, the crystallization activation depends on a random unintentional seeding event, for example a crystalline dust or an incomplete fusion. It has been shown that adding a seeding step to the thermal discharge protocol in a stirring crystallizer results in a quick and reproducible crystallization. The efficiency of the crystallization process will therefore depend on two mechanisms: the seeding step and the agitation quality. Future work will focus on a parametric study of these two mechanisms. The integration of a bubbling and seeding system in a real LHTES demonstrator will also be proposed.

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