

Article

# Nucleation Triggering of Highly Undercooled Xylitol Using an Air Lift Reactor for Seasonal Thermal Energy Storage

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**Featured Application:** A potential application of this work consists in using Xylitol as phase change material for latent heat thermal energy storage at temperatures varying from ambient up to slightly below 100 °C.

**Abstract:** Bio-based glass-forming materials are now considered for thermal energy storage in building applications. Among them, Xylitol appears as a biosourced seasonal thermal energy storage material with high potential. It has a high energy density and a high and stable undercooling, thus allowing storing solar energy at ambient temperature and reducing thermal losses and the risk of spontaneous nucleation (i.e., the risk of losing the stored energy). Generally when the energy is needed, the discharge triggering of the storage system is very difficult as well as reaching a sufficient power delivery. Both are indeed the main obstacles for the use of pure Xylitol in seasonal energy storage. Different techniques have been hence considered to crystallize highly undercooled Xylitol. Nucleation triggering of highly undercooled pure Xylitol by using an air lift reactor has been proven here. This method should allow reaching performances matching with building applications (i.e., at medium temperatures, below 100 °C). The advantages of this technique compared to other existing techniques to activate the crystallization are discussed. The mechanisms triggering the nucleation are investigated. The air bubble generation, transportation of nucleation sites and subsequent crystallization are discussed to improve the air injection operating conditions.

**Keywords:** energy discharge; bubbles burst; bubbles transportation; crystal growth rates; undercooling

## 1. Introduction

One of the key elements to optimize the use of renewable energies and to improve building performances is the development of thermal energy storage [1–5]. To this purpose, latent heat storage using phase change materials (PCMs) is known to provide a greater energy density than the sensible heat storage with a smaller temperature difference between the energy charge and the energy discharge. Cabeza et al. [6] reviewed many of PCM complying with this application as well as the eventual associated technical problems as separation, segregation, corrosion, and materials compatibility. Among inorganic systems such as salts and salt hydrates, organic compounds such as paraffin waxes, fatty acids or esters and polymeric materials [3–5], sugar alcohols (SAs) are promising phase change materials for seasonal energy storage applications at low to medium temperatures (below 100 °C) and allow avoiding these technical problems.

These bio-based glass-forming materials have been up to now widely studied in food engineering and pharmaceuticals [7,8]. Recently, they have been also studied for thermal energy storage applications [9–14]. The idea consists in storing thermal energy into undercooled sugar alcohols at a temperature inferior to their melting one, as close as possible to the ambient temperature, to reduce thermal losses and to limit the risk of spontaneous energy discharge. When heating is needed, the storage system is discharged by triggering sugar alcohols nucleation, which is the first step of crystallization.

In spite of the fact that Xylitol has been identified as one of the most promising candidates among sugar alcohols for applications at temperature below 200 °C due to its high energy storage potential, few studies only have been conducted on it, as reported in [15,16]. Its melting point of 95 °C, its latent heat superior to 263 J·g<sup>-1</sup> and its total energy density 4–5 times higher than that of water (110–150 kWh·m<sup>-3</sup> whereas it is approximately 30 kWh·m<sup>-3</sup> for water on a seasonal basis) are well suitable for their use in cheap solar collectors for instance. However, the strong undercooling behavior of Xylitol as well as its nucleation triggering which is very difficult due to the very high activation energy required for atomic rearrangements at the liquid–solid interface (i.e., the energy barrier to trigger the nucleation) are seen as the major obstacles to their employment as PCM. A decrease in temperature causes indeed a drastic increase in viscosity making the atom diffusion slow down or even stop. This is the reason why [15], among others, stipulated the impossibility to solidify pure Xylitol once at liquid state and thus, stopped their investigation about this material.

In the case of undercooled Xylitol, the crystallization step is thus a challenging process since it has a very high viscosity at ambient temperature (see the evolution of its viscosity versus temperature in [17]). Indeed, the transition from liquid to solid comes with a conformation change (from a linear structure in the liquid phase, to a bent one in the solid phase) which increases the required energy to overcome the activation energy barrier. These are the reasons why Xylitol crystal growth rates are low at ambient temperature. The rate values were measured and calculated according to temperature and presented in [18]. The maximum growth rates appear around 50–55°C and are of the order of magnitude of μm·s<sup>-1</sup>.

In this work, it is shown that these characteristics are, on the one part, an asset for a medium/long term storage. Indeed, the probability for spontaneous nucleation is negligible at high undercoolings which leads to a negligible risk of losing the stored energy and limited thermal losses. On the other part, the nucleation triggering, i.e., of the discharge triggering when the energy is needed, is very difficult and the crystal growth rates are too low for an efficient power delivery. Consequently, if these two main obstacles are overcome, Xylitol would be a very competitive phase change material for seasonal storage applications at low to medium temperatures, particularly in building field. To this end, an air lift reactor was designed and the proof of concept enabling to reach performances matching with building applications is described in [19].

This work aims at comparing the advantages of using an air lift reactor with the other potential techniques able to activate highly undercooled pure Xylitol nucleation and to accelerate its complete crystallization. These latter techniques include local cooling, intentional seeding, ultrasonication, and mechanical agitation.

A preliminary parametric study in order to identify the key variables influencing these mechanisms is performed. To do so, air bubble generations, transportations of nucleation sites and subsequent crystallizations are observed and discussed. This understanding should help to identify the parameters triggering nucleation at any time (or temperature) and to crystallize the entire product in due time.

## 2. Attempts of Nucleation Triggering and of Discharge at an Acceptable Power

### 2.1. Materials

Xylitol was purchased from Roquette (batch E089X, purity 98.43%, Lestrem, France). In all the performed experiments, molten Xylitol is conditioned as follows: Xylitol is placed at 100 °C overnight in an oven to be fully melted, then, it is free-cooled down to the starting temperatures (ranging from 30 °C to 75 °C).

### 2.2. Xylitol-Conscious Nucleation and Crystallization: Commonly Used Techniques

The most common used techniques to crystallize Xylitol have been considered and the preliminary observations and analyses carried out are presented hereafter.

1. Local cooling. It fails to trigger nucleation in severely undercooled Xylitol due to the very high activation energy required for atoms diffusion and rearrangement at the solid–liquid interface.
2. Intentional seeding. It allows triggering Xylitol crystallization, even in cases with very high undercooled melts. However, the effect of seeding on nucleation is too local. The seed growth being too slow (4 days/10 mL), this technique will lead to very low heat release rates and too long discharge times for the aimed application.
3. Ultrasonication. High-power ultrasonication (450 W) allows also crystallizing the studied Xylitol. However, the crystallization rates are still too low for this technique to become appropriate at the storage system scale.
4. Solvents addition in Xylitol. It does not contribute to accelerate crystallization even in combination with ultrasonication.

### 2.3. Successful Xylitol Nucleation and Crystallization: Preliminary Tests

Two techniques only succeeds in activating the nucleation of severely undercooled melts in extended area with then, significantly increased crystallization rates of the studied systems.

The first one is the mechanical agitation and the second one consists in stirring undercooled Xylitol by bubbling. Both of them aim at triggering Xylitol nucleation and at speeding-up its crystallization.

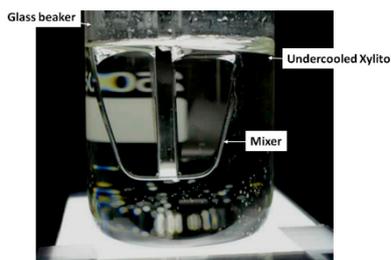
#### 2.3.1. Undercooled Xylitol Crystallization Induced by Mechanical Agitation

In industrial crystallization, mechanical agitation is often used in combination with seeding. The primary objectives of this method are to create and maintain a good dispersion of the seeds in the bulk and to enhance the rate of mass transfer between the solid and liquid phases [19]. Mechanical agitation without seeding has been here considered to crystallize undercooled Xylitol.

A glass beaker with a diameter of 85 mm and a height of 105 mm is filled with Xylitol initially in powder form and placed into an oven up to its molten liquid state. Small volumes (~400 mL) of undercooled Xylitol are used for testing. Then, the beaker is put out of the oven and remains at room temperature to make it naturally cool down to the selected starting temperature. Finally, the mixer is started with a power of 125 W at a constant and low speed and for a short duration of 5 s. This allows the agitation of the undercooled Xylitol.

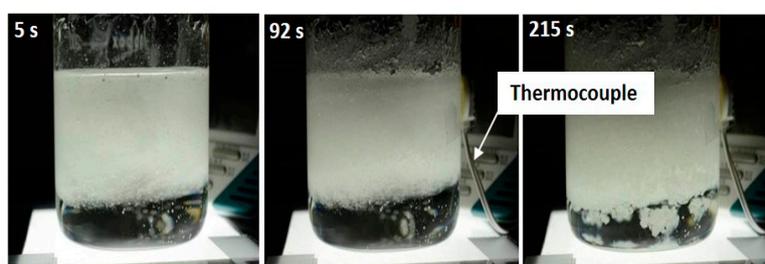
The form and the position of the mixer within the undercooled Xylitol can be seen in Figure 1. The crystallization of the sample is observed with a high speed CCD camera (HM1024, Genie, Teledyne DALSA, Waterloo, ON, Canada). Simultaneously, a thermocouple glued to the wall of the beaker provides useful information regarding the sample temperature evolution with time. Several starting temperatures were investigated.

Figure 1 illustrates the device used for mechanical agitation and the snapshots in Figure 2 show an example of tests performed on highly undercooled melts at a starting temperature of 50 °C ( $T_0 = 50$  °C), i.e., with an undercooling of 45 °C ( $\Delta T = 45$  °C) regarding the melting temperature of 95 °C.



**Figure 1.** Picture of the mixer within a sample of undercooled Xylitol in a glass beaker at a starting temperature  $T_0 = 50\text{ }^{\circ}\text{C}$  ( $\Delta T = 45\text{ }^{\circ}\text{C}$ ) before mechanical agitation.

It has been observed that mechanical agitation results in a very fast response. Indeed, nucleation is reached in only 5 s of mixing all over the agitated region. Then, the crystallization progresses downwards from the agitated region. As shown in Figure 2, crystal clusters detach from the crystallization front and fall by gravity, thus contributing to accelerate the process of crystallization. After 1 min 30 s an increase in temperature of the beaker exterior wall is measured ( $25\text{ }^{\circ}\text{C}$ ).



**Figure 2.** Snapshots of an undercooled Xylitol sample in a glass beaker at a starting temperature of  $T_0 = 50\text{ }^{\circ}\text{C}$  ( $\Delta T = 45\text{ }^{\circ}\text{C}$ ) after mechanical agitation. Observation of its crystallization after 5, 92, and 215 s.

The obtained results suggest that mechanical agitation could be an efficient solution for discharging the storage system when necessary and at appropriate speeds. However, this technique shows a solidification which is less homogeneous from a spatial viewpoint than the bubbling one (Figure 2 versus Figure 3). Besides, the mechanical agitation is intrusive, and would require a specific reactors design and would probably lead to a significant extra-cost.

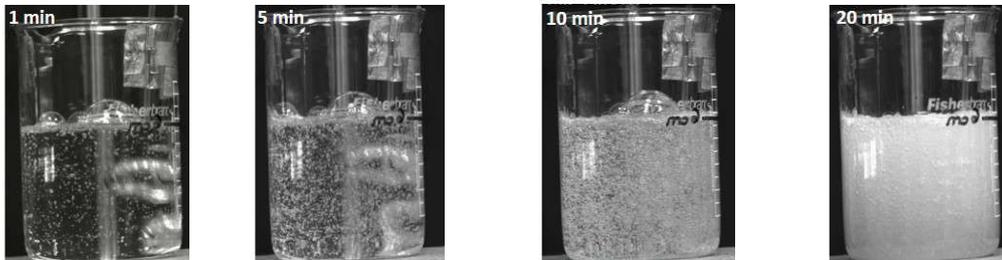
### 2.3.2. Stirring by Bubbling

As mechanical agitation, bubble stirring allows activating the nucleation of highly undercooled Xylitol in extended area. To this purpose, bubble columns are widely employed within chemical industry as gas–liquid contactors and multiphase reactors. Examples of applications of this reactor type include oxidations, hydrogenations, fermentations, and the production of synthetic fuels [20]. One of the main features of bubble column operation is that gas and liquid or suspended solid phases are brought in contact without the need for additional mechanical stirring equipment, making bubble column design and operation appear easier than that of other gas–liquid reactors. The gas distributor is usually located at the bottom of the column, while the liquid phase can either be distributed co-currently or counter-currently with respect to the flow direction of the gas phase.

Bubbling with air has been considered as an alternative to mechanical agitation to induce Xylitol crystallization. Contrary to mechanical agitation, bubbling is a low-intrusive technique, consequently, easy to implement in standard storage containers and hence cost effective [21].

The same previous conditions (glass beaker, Xylitol and protocol to prepare the undercooled Xylitol) have been used. Only the technique of nucleation triggering is different from the previous tests. The air distributor is a flexible pipe of 3 mm inner diameter which is connected to a small pump. The air inlet is located at the bottom of the column and the air flow is of  $80\text{ L}\cdot\text{h}^{-1}$ .

After 30 min, an increase in Xylitol temperature is measured (35 °C) within the beaker. The snapshots in Figure 3 show that air injection at the bottom of the beaker fosters Xylitol nucleation as well the crystallization progress over time in a complete different way than that from the one obtained using mechanical agitation. In this case, crystals form around air bubbles all over the stirred area.



**Figure 3.** Snapshots of the undercooled Xylitol crystallization induced by air bubbling in a glass beaker at different times (air flow rate = 80 L/h; Starting Temperature  $T_0 = 50$  °C, undercooling degree  $\Delta T = 45$  °C).

The possibility to induce the undercooled Xylitol crystallization by bubbling using a simple and cost effective technique has been proven through this experiment. The further researches carried out in order i/ to understand the effect of bubbling on crystallization, ii/ to identify the key related variables and iii/ to improve air injection operating conditions are presented in next section.

### 3. Undercooled Xylitol Crystallization Induced by Bubbling

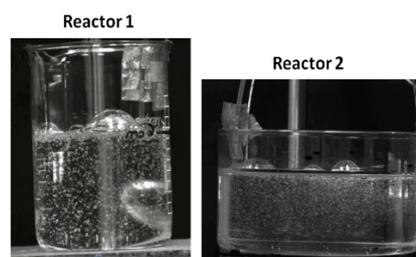
A significant amount of research works on bubble columns regarding bubble formation and bubble rise velocity aspects, flow patterns characteristics and parameters, heat and mass transfers, columns design, and operating conditions has appear in literature in the last few decades (see e.g., recent reviews [22–24]), including experimental and numerical studies.

However, to the best of knowledge, the use of bubbling to trigger the nucleation of undercooled melts and to accelerate their crystallization rates has never been studied.

#### 3.1. Air Lift Reactors

Two different liquid/gas reactors have been used to achieve an overall understanding of the Xylitol crystallization by bubbling, as can be seen in Figure 4:

- *Reactor n°1.* The reactor is a cylindrical glass beaker with a diameter of 85 mm and a height of 105 mm, filled with the molten sugar alcohol (SA) up to 60 mm of height. Air bubbles are generated at the bottom of the vessel by a single tube connected to a pump. The inner diameter of the tube is 3 mm. The pump can provide an air flow rate of  $80 \text{ L}\cdot\text{h}^{-1}$ .
- *Reactor n°2.* The reactor is a cylindrical glass crystallizer with a diameter of 140 mm diameter and a height of 105 mm, filled with the molten SA up to 60 mm of height. As in reactor n°1, air bubbles are generated at the bottom of the vessel by a single tube (3 mm inner diameter) connected to a pump ( $80 \text{ L}\cdot\text{h}^{-1}$ ).



**Figure 4.** Pictures of the 3 used air lift reactors (diameter × height mm): n°1 (85 × 105 mm) and n°2. (140 × 105 mm).

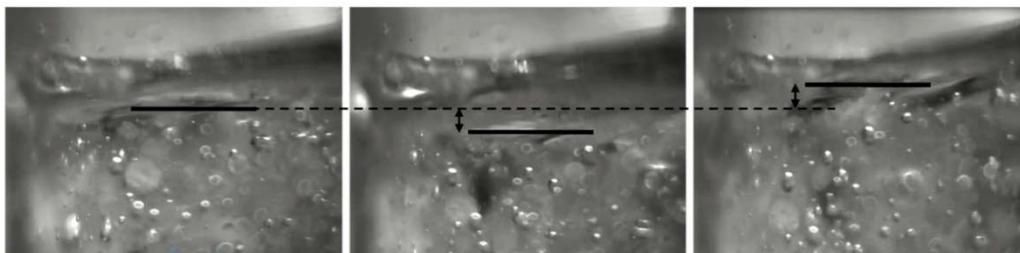
The same preparation protocol described in Section 2 is applied to Xylitol. Once the desired starting temperature is reached, the bubbling is started and its impact on the SA crystallization process is visualized by using a high speed CDD camera.

### 3.2. Bubbles Observation into Molten Xylitol

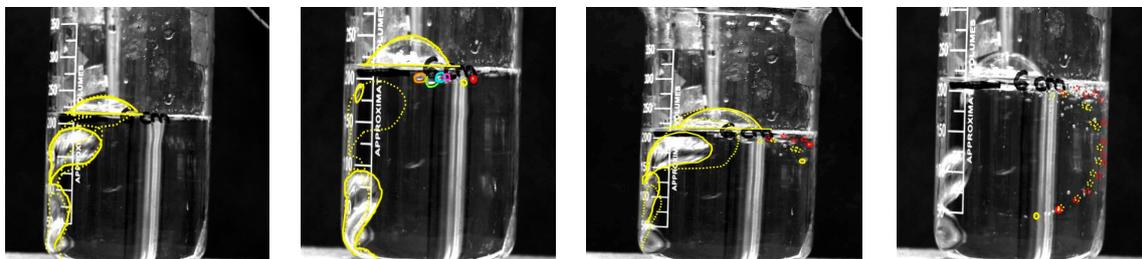
Numerous experiments have been performed in order to get an overall view of the crystallization process by bubbling. Most of them were carried out in reactor n°1. The air flow is still of  $80 \text{ L}\cdot\text{h}^{-1}$  and the starting temperature of the melt ( $T_0$ ) varies from  $30 \text{ }^\circ\text{C}$  to  $75 \text{ }^\circ\text{C}$ . The snapshots in Figure 3 show the different stages of bubbling from the side whereas the top views are shown in figure 4. The initiation and the progress of the crystallization in the experiment carried out at  $50 \text{ }^\circ\text{C}$  (i.e., undercooling degree  $\Delta T = 45 \text{ }^\circ\text{C}$ ) is the same whatever the applied initial thermal conditions.

The crystallization process follows the next steps:

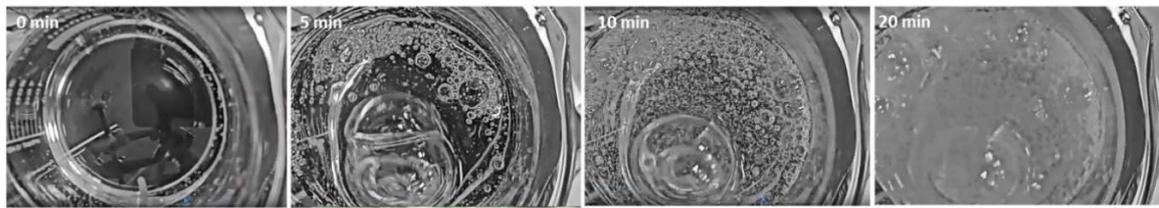
- Bubbles are formed continuously at the submerged orifice. First they grow, detach from the orifice and rise in the melt up to the liquid free-surface. The bubbles generation is periodic and induces an oscillatory motion of the liquid, with a major circulation cell which fills the entire column. Snapshots in Figure 5 illustrates the beat of the free-surface of the liquid.
- At the free-surface of the liquid, the bubbles burst in a very short time and generate smaller bubbles (see Figure 6 (colored circles)). Part of these smaller bubbles are caught by the fluid and dragged by the flow cell as shown in Figure 6. As it can be seen in Figure 7, the small bubbles are then dispersed within the liquid and their amount increases with time.
- After an average stirring time of 5 min of the mixture “bubbles/Xylitol”, Xylitol starts to crystallize. Crystallization begins on the surface of the bubble, at the interface air/Xylitol, then it progresses in the outward direction forming a spherical solid shell.



**Figure 5.** Oscillation (up and down motion) of the free-surface of the liquid with time produced by the periodic bubbling.



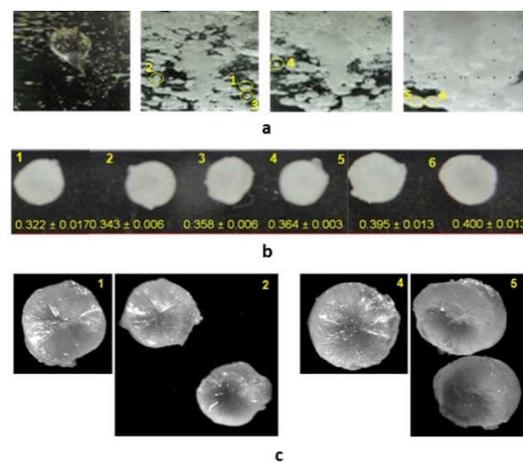
**Figure 6.** Pictures of the initial stages of bubbling when the small bubbles created at the free surface are captured by the liquid and entrained in its movement. Bubbles dragged by the liquid flow are highlighted by yellow and red circles.



**Figure 7.** Top view pictures of bubbles reaching the free-surface of the liquid at different times of the crystallization process. The bubbles burst and generate small daughters.

Different stages of the crystallization process from the bubbling in the undercooled melt to a quite advanced stage of the crystallization process are presented in Figure 8a. Numerous spherical solid white particles can be observed in suspension.

Six of them with a diameter inferior to 0.5 mm have been extracted as can be seen in Figure 8b. Magnified pictures of the cross-section of two particles showing the presence of a hole in the center of each sphere are presented in Figure 8c. The hole corresponds to the air bubble on which crystallization has been initiated.



**Figure 8.** Xylitol crystallization pictures: (a) small air bubbles are dragged by the liquid circulation cell then white solid particles are formed by crystallization of Xylitol on the air bubbles surface. Finally, numerous solid particles can be observed in suspension; (b) Pictures of 6 particles extracted from the beaker and measured using a caliper (dimensions are given in millimeters); (c) magnified pictures of the cross-sections of particles cut in half.

An air injection allows the occurrence of air bubbles and of a flow cell into the molten Xylitol both observed for reactors 1 and 2. These phenomena participate to the formation and the spreading of crystallized Xylitol particles.

The bursting of the primitive air bubbles at the free liquid surface with production of small bubbles acting as nucleation sites appear, indeed, as a necessary condition for the crystallization of undercooled Xylitol.

The efficiency of the crystallization process depends thus on (i) the number of the produced nucleation sites; as well as (ii) the extent and the homogeneity of their dispersion within the melt.

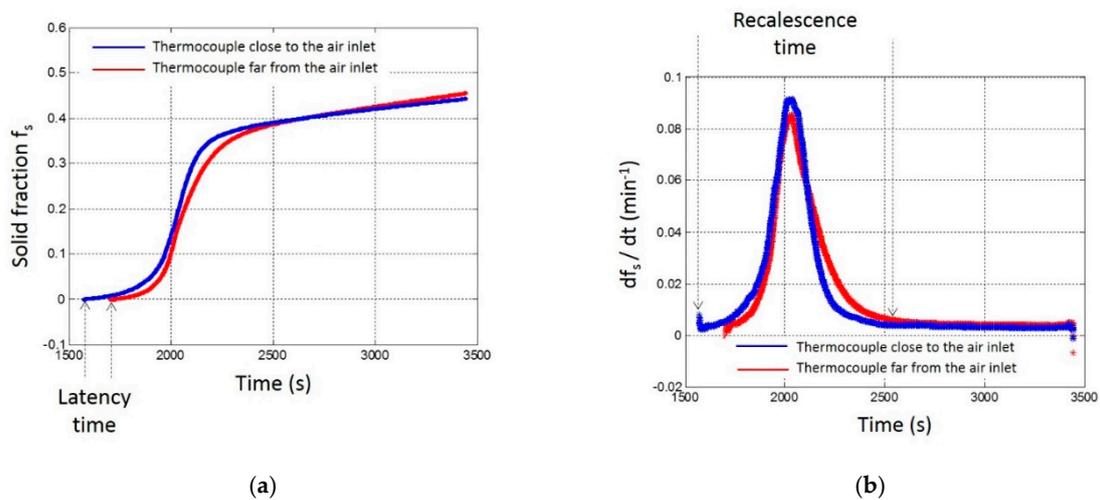
Next section is consequently dedicated to the preliminary thermal study of the previous described experiments but the glass beaker filled with undercooled Xylitol is, this time, thermally insulated.

#### 4. Preliminary Thermal Analysis as a Proof of Feasibility

Bubbling is started once the desired starting temperature is reached. The thermal response of Xylitol during bubbling is recorded by two thermocouples: one close to the tube injecting air and the other one placed on the opposite side. The air is injected at room temperature (20 °C).

A typical thermal response of high undercooled Xylitol during bubbling is in Figure 9 where three different periods can be clearly distinguished:

- *The induction period*, from the beginning of bubbling to the beginning of crystallization. In a perfectly adiabatic reactor, the temperature of the melt should be constant during this period. In practice, it slightly decreases due to thermal losses. Thermal losses take place both, by conduction through the reactor wall and by convection due to air bubbling at ambient temperature.
- *The recalescence period*, where Xylitol is crystallizing and its temperature raises. In a perfectly thermally insulated system, Xylitol should reach the melting point and the crystallization process should stop at that moment. However, due to thermal losses, the maximum temperature reached by Xylitol is inferior to its melting point and the crystallization can progress beyond this point. We consider in the following that the recalescence period ends when Xylitol reaches its maximum temperature.
- *The end-period*, where crystallization (if any) is driven by heat extraction due to thermal losses.



**Figure 9.** Time evolution of the solid fraction (a) and time behavior of the crystallization rate (b) calculated from the temperature data obtained using both thermocouples.

From the recorded temperature data, the evolution of the solid fraction over time as well as the total crystallization rate can be estimated. It has been shown in [19] that the solid fraction ( $f_s$ ) can be estimated the following equation:

$$\frac{df_s}{dt} = \left( \frac{c_p}{L_m} \right) \left[ \frac{dT}{dt} + k(T - T_\infty) \right] \quad (1)$$

where  $c_p$  is the specific heat of Xylitol,  $L_m$  is the latent heat and  $k$  the thermal exchange coefficient. Once,  $c_p$ ,  $L_m$  and  $k$  parameters are known, the crystallization rate ( $df_s/dt$ ) can be determined.

An example of the estimated time evolution of the crystallization rate as well the solid fraction corresponding to temperature data recorded by both thermocouples are depicted in Figure 9.

It can be seen that the crystallization progresses slowly at the beginning, then accelerates up to a maximum crystallization rate, and the rhythm of crystal production reduces afterwards. At the end of the recalescence period ( $t \approx 2500\text{s}$  in Figure 9), the crystallization rate is such that power delivered by solidification equals the thermal losses.

These results confirm the possibility of using Xylitol as phase change material for seasonal thermal energy storage despite its high viscosity and by using a simple, non-intrusive and thus cost-effective bubbling technique.

Further works will consist in studying the bubbling performances for thermal storage applications. Quantitative analyses will be performed to estimate the thermal properties influencing the discharge process and to evaluate the reachable performances.

## 5. Conclusions

Xylitol high and stable undercooling allows long-term thermal energy storage at low to medium temperatures with reduced thermal losses and with negligible risk of spontaneous energy discharge. However, its nucleation triggering (energy discharge triggering) and hence, its subsequent crystallization rates (discharge power delivery) have been recognized as major obstacles to its use as PCM for applications below 200 °C such as building applications.

Using an air lift reactor is a very promising technique to discharge the storage system at the required power when needed.

In this paper, the proof of the concept was achieved by using pure Xylitol, i.e. without adding any additives. This paper provides a better understanding of the effect of primitive bubbles burst and small bubbles transportation on nucleation triggering of the whole highly undercooled Xylitol in a small container. Indeed, it has been shown that Xylitol nucleation occurs on the surface of the small bubbles generated at the liquid surface when primitive bubbles burst. Once dispersed within the reactor by the liquid flow, they act as nucleation sites. The bursting of the primitive bubbles at the free liquid surface with production of smaller bubbles is hence a necessary condition for Xylitol crystallization. As mechanical agitation, stirring by bubbling is able to trigger the nucleation of Xylitol in extended and highly spatially resolved areas. The efficiency of the crystallization process will be obviously dependent on the number of nucleation produced sites as well as the extent and the homogeneity of their dispersion within the melt. Besides, this technique is a low intrusive technique and, consequently, easy to implement in standard storage containers. The feasibility of nucleation triggering thanks to an air lift reactor bubble stirring being proven in this paper, further works will consist in providing an in-depth understanding of highly undercooled Xylitol crystallization induced by air injection, including bubbles formation and characteristics, nucleation sites generation, nucleation sites dispersion, and crystallization on the liquid/gas interfaces. Further works will also consists in studying the air injection performances for thermal energy storage applications to pave the way for bubbling conditions optimization.

**Author Contributions:** All authors contributed to this work. Conceptualization, M.D., A.G. and E.P.D.B.; methodology, M.D. and A.G.; investigation, M.D., A.G. and E.P.D.B.; data curation, M.D., A.G. and E.P.D.B.; writing—original draft preparation, E.P.D.B.; writing—review and editing, M.D. and A.G.; visualization, M.D. and A.G.; supervision, E.P.D.B.; project administration, E.P.D.B.

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