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Novel crystal morphology for sodium bicarbonate obtained by using the supercritical anti-solvent process

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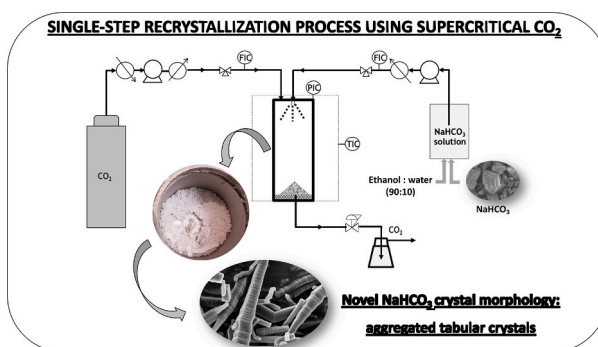
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HIGHLIGHTS

- Implementation of a single-step process of sodium bicarbonate recrystallization using supercritical CO₂
- Formation of a novel crystal morphology: long and thick zigzag shapes
- A mechanism of Crystallization by Particle Attachment (CPA) suggested

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to develop a sustainable single-step process involving supercritical CO₂ as an anti-solvent to recrystallize sodium bicarbonate from an aqueous solution. First, a feasibility study validated the capacity to recrystallize sodium bicarbonate from a hydroalcoholic solution, under a pressure of at least 150 bar, an atomization jet solution velocity of at least 2.6 m·s⁻¹ and a mass flowrate ratio X (CO₂ over solution) of at least 21.6. The crystals obtained were long, thick and zigzag-shaped. In a second step, an optimization of operating conditions was proposed to obtain crystals exhibiting an isometric habit. The most favourable conditions leading to the thickest and shortest crystals were 150 bar, 50 °C, an atomization velocity of 2.6 m·s⁻¹, and a solute concentration of 0.45 g·(kg_{solvent})⁻¹. No significant influence of higher pressure or higher atomization velocity was observed.

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1. Introduction

Sodium bicarbonate NaHCO_3 is a water-soluble inorganic compound mainly encountered in the form of white powder. This material in its crystalline form is used for many applications: pharmaceutical and medical applications, cosmetics, food and feed usage, or in the field of cleaning and hygiene (antimicrobial, antifungal, ...) [1,2]. Depending on the applications, specific grade, and crystal properties such as specific surface area and/or crystal habit are sought-after. To control those properties, it is necessary to master the crystallization process. Sodium bicarbonate crystals are generally obtained by bubbling CO_2 in an ammonia-rich aqueous solution of sodium chloride, or in a saturated solution of sodium bicarbonate [3]. The formation of crystals and the control of their properties through this means are well-known today. Nevertheless, new ways of (re)crystallization could be explored in view to obtain new sodium bicarbonate properties for novel applications.

The aim of this study is to explore the recrystallization of sodium bicarbonate from an aqueous solution using supercritical carbon dioxide (scCO_2). Over the last 30 years, processes using scCO_2 have received increasing attention. Indeed, such processes involve CO_2 which is recognized as a safe solvent, respectful to the environment in comparison with commonly used liquid organic solvents. In addition, CO_2 is a co-product of the chemical industry, mainly co-produced in the ammoniac and cement industries. Therefore, the use of CO_2 as a supercritical fluid meets the requirements of industry 4.0 and finds its proper place in the circular economy. The specific physico-chemical properties of scCO_2 and mainly its density and diffusivity, which vary significantly according to the operating conditions of pressure and temperature, lead to the implementation of efficient processes for many applications including particle generation. The mild critical properties ($P_c = 73.8$ bar and $T_c = 31.1$ °C) and particularly the low critical temperature allow to process thermosensitive compounds. Finally, CO_2 being gaseous under ambient conditions, it is spontaneously separated from the processed materials which are solventless and can be utilized directly [4]. It is worth highlighting that the post-crystallization operations of separation required for recrystallizations in liquid solutions can thus be skipped and that a reduced number of operations in a crystallization process then limits the possibility of crystal property evolution.

The scCO_2 processes implemented for particle generation are therefore compact and allow the formation of particles with controlled properties such as size, particle size distribution and polymorphism. Different crystallization methods can be used depending on the role played by scCO_2 towards the solute to precipitate: if the solute is soluble in scCO_2 , it is possible to perform the precipitation using rapid expansion from supercritical solution processes (RESS); if the scCO_2 has a low affinity for the solute, the precipitation may be performed using supercritical anti-solvent (SAS) processes. A third way consists in using scCO_2 as a solute in particles from gas-saturated solution processes (PGSS) [5].

Since sodium bicarbonate is not soluble in scCO_2 , the SAS process thus seems to suit well for its precipitation. The SAS process consists in atomizing a solution containing the solute dissolved in a solvent through a capillary or a nozzle into an autoclave in which a constant flow of scCO_2 circulates at set temperature and pressure. During the operation, the solution is sprayed in small entities into a continuum of scCO_2 . The solvent and the scCO_2 should be miscible in all proportions under the chosen operating conditions, but the scCO_2 should act as an antisolvent for the solute. The solvent diffuses towards the scCO_2 -rich phase whereas scCO_2 diffuses in the dispersed liquid phase, playing the role of an anti-solvent regarding the solute which finally precipitates. The parameters that have an influence on the powder characteristics are temperature, pressure, CO_2 and solution flow rates, nature of the solvent, and solute concentration in the solution. This process allows the formation of small size particles (from 10 nm to 100 μm) with controlled powder characteristics and polymorphic nature [6]. In literature, SAS processes were mainly applied to pharmaceutical molecules [7] and polymers.

Regarding inorganic compounds, supercritical fluid processes can fall into two categories depending on whether the treatment involves a physical transformation or a chemical reaction. Most of the works reported in the literature deal with the synthesis in supercritical media for material processing. Over the last three decades, works on the implementation of the synthesis in a supercritical medium of semi-conductors, carbons, metals, oxides, and nitrides [8] have been described. The combination of the SAS process with the synthesis have also been performed for ceramic oxides [9] or for titanium oxide [10].

In this work, the SAS process has been applied for the recrystallization of sodium bicarbonate from an aqueous solution targeting a crystalline form with novel properties.

The most encountered solvent for sodium bicarbonate solutions is water. Sodium bicarbonate is indeed soluble in water, nevertheless water has a low solubility in scCO_2 [11]. The challenge here was then to achieve the water intake in the scCO_2 flow during the SAS process. Hence, a third compound or so-called cosolvent for which both water and scCO_2 have an affinity, but having a low affinity with sodium bicarbonate should be added to help water removal and prevent the resolubilization of the solute in the fluid phase. Ethanol seemed to be a good candidate. Indeed, Prosapio et al. [12] used a supercritical CO_2 antisolvent process to precipitate bovine serum albumin from an aqueous solution. In this work, the authors investigated ethanol, acetone and isopropyl alcohol as cosolvent to successfully obtain microparticles and thus remove water.

The purpose of this work is thus to check the feasibility of the precipitation of sodium bicarbonate previously dissolved in an aqueous solution using scCO_2 as an antisolvent and to find the optimal operating conditions leading to small crystals with a morphology of interest. Temperatures of 40 and 50 °C, pressures from 120 to 180 bar, mass ratios of CO_2 and solution flow rates from 15 to 25, solution velocities in the capillary of 2.6 and 4.2 $\text{m}\cdot\text{s}^{-1}$, and solution concentrations from 0.29 to 0.9 $\text{g}\cdot(\text{kg}_{\text{solvent}})^{-1}$, were used to delimitate an operating domain for which the precipitation of sodium bicarbonate could be possible.

2. Materials and methods

2.1. Chemicals

Sodium bicarbonate was provided by the company Solvay (France). The product was in the form of a white powder with a mean particle size of an average of 50 μm (Fig. 1). CO_2 (purity 99.7%) was supplied by Air

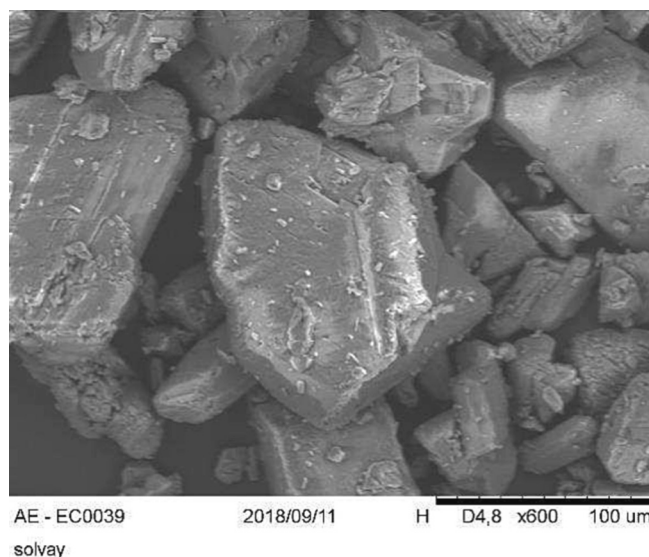


Fig. 1. SEM image of the initial powder of sodium bicarbonate to be recrystallized.

Liquide Méditerranée (France). Distilled water used to solubilize the sodium bicarbonate was produced at the laboratory using a distillatory vessel / apparatus. Absolute ethanol (purity 99.8%) and technical ethanol (96%) came from Fisher (France).

2.2. Supercritical anti-solvent apparatus

The following set-up and procedure are described in the case of absolute ethanol used as a cosolvent. The operation is the same with other cosolvents.

The set-up (Fig. 2) is composed of a CO₂ tank, a cryogenic bath, a high-pressure pump (Separex, France) and a liquid pump (Gilson, France) dedicated to the circulation of CO₂ and the sodium bicarbonate solution, respectively. The precipitation takes place in an autoclave (50 mm internal diameter × 700 mm height) which is equipped with a double jacket in which temperature-controlled water circulates. The autoclave is divided into two in the middle with a metallic basket equipped with a frit placed in the upper part. The micronized powder is collected in the basket. The lower part of the autoclave is used to recover potential drops of liquid preventing their contact with the powder.

The scCO₂ and the sodium bicarbonate hydroalcoholic solution entered co-currently through the top of the autoclave. The liquid solution was injected through a capillary. At the middle of the autoclave, just below the frit, an exit for the CO₂ was installed. At the end of this tubing after a depressurization valve, a solvent trap was placed to recover the condensed solvent. Some pressure and temperature sensors were placed at different points of the process.

The procedure used to recrystallize sodium bicarbonate is as follows: CO₂ is first introduced under targeted pressure, temperature, and flow rate. This supercritical flow rate should be maintained constant using the exit valve during the whole experiment. When a steady state is reached, absolute ethanol is introduced through the capillary during the equivalent of one residence time. The absolute ethanol is then replaced by the sodium bicarbonate hydroalcoholic solution during the experiment time. At the end of the experiment, absolute ethanol is once again injected to eliminate solute traces from the capillary and decrease the water content in the autoclave. Indeed, while sodium bicarbonate is very soluble in water, it is weakly soluble in absolute ethanol; there is therefore little likelihood that the precipitated sodium bicarbonate be resolubilized in the medium during this stage. Then, the absolute ethanol injection is stopped, and the autoclave is flushed by pure scCO₂

maintaining constant pressure, temperature, and flow rate during the equivalent of two residence times to completely remove the solvent (ethanol and possibly water traces). Finally, the high-pressure pump is stopped, and the autoclave is depressurized. Once the autoclave has reached the atmospheric pressure, the sodium bicarbonate powder is recovered and characterized.

2.3. Characterization methods

Powders were analysed by Raman spectroscopy to ensure that pure sodium bicarbonate was precipitated. Moreover, all the precipitated powders were observed by Scanning Electron Microscopy to determine the crystal habit and mean size.

2.3.1. Raman spectroscopy

The sodium bicarbonate powders were submitted to Raman spectroscopy to guarantee that the powder is only constituted of sodium bicarbonate and does not contain other solid phases coming from the sodium bicarbonate degradation.

The apparatus was a Labram HR (Horiba Jobin Yvon). The conditions of acquisition were as follows: laser wavelength 514 nm, objective ×50, numerical aperture 0.5, acquisition time 300 s. 3 to 4 zones were tested on each sample. A power test was done to check that the laser does not modify the sample. Table 1 gives the Raman shifts δ corresponding to the sodium bicarbonate NaHCO₃ and to the other solid phases due to NaHCO₃ degradation: Na₂CO₃ · H₂O, Na₂CO₃ · 3 NaHCO₃, and Na₂CO₃ · NaHCO₃ · 2 H₂O.

Table 1
Raman shifts corresponding to sodium bicarbonate NaHCO₃ and to its degradation solid phases.

Solid phase	Raman main shifts δ (cm ⁻¹)
Na ₂ CO ₃	1080
Na ₂ CO ₃ · H ₂ O	1069
Na ₂ CO ₃ · 3 NaHCO ₃	1021; 1031; 1056
Na ₂ CO ₃ · NaHCO ₃ · 2 H ₂ O	1061
NaHCO ₃	1046; 1268

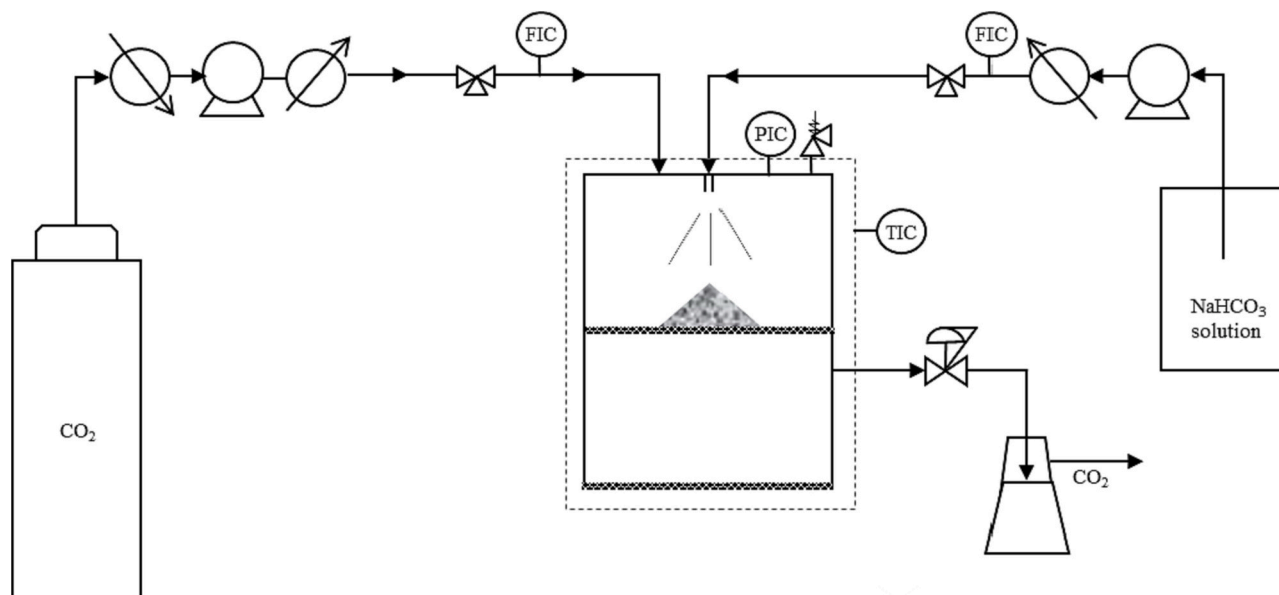


Fig. 2. Supercritical Anti-solvent apparatus.

2.3.2. Scanning electron microscopy

Some observations were performed using a Scanning Electron Microscope Hitachi TM3000 Tabletop at 15 kV. The precipitated powder was stuck on plots covered with an adhesive patch. Some of the samples were metalized with a fine layer of Au—Pd. The average size of the stick shape crystals was determined from our observations. About 10 randomly chosen sticks from more than 10 SEM photographs were considered for this estimation.

Some observations at higher magnification ($\times 30,000$) were made using a Scanning Electron Microscope Hitachi S-4800 at 5 kV. Samples were prepared on plots covered with an adhesive patch after they were metalized with a fine layer of Au—Pd.

3. Results and discussions

First assays were carried out to check if the SAS process could be used for the precipitation of sodium bicarbonate from an aqueous solution. In the first steps, the cosolvent was chosen and the ternary system water/cosolvent/ CO_2 was studied in order to identify the optimal cosolvent content to ensure miscibility between CO_2 and water. Then, SAS experiments were carried out varying several operating parameters: pressure, and more particularly the atomization velocity of the sodium bicarbonate solution and the flowrate mass ratio X corresponding to the mass flow rate of CO_2 divided by the mass flow rate of sodium bicarbonate solution. Once the feasibility was proven, an optimization stage was carried out by studying the influence of operating parameters pressure, temperature, concentration of the solution, and flowrate mass ratio X on the habit and size of the produced crystals.

3.1. Feasibility of the SAS process for the reprecipitation of sodium bicarbonate from an aqueous solution

Sodium bicarbonate has a certain solubility in water, but it is not possible to precipitate sodium bicarbonate from such an aqueous solution in scCO_2 using the SAS process because the solubility of water in CO_2 is too low [11] even under high pressure and temperature. The use of a third body with an affinity for both scCO_2 and water should be considered.

The first step of this work was to select the best cosolvent to use to ensure miscibility between water and CO_2 under the SAS process operating conditions. The second step was to determine the mass proportion of cosolvent to use in the sodium bicarbonate aqueous solution to achieve the water removal and therefore the solid precipitation. The third step was to perform SAS experiments and to determine suitable operating conditions allowing precipitation.

3.1.1. Choice of the most suitable cosolvent

Through phase equilibrium data found in the literature, several cosolvents were considered to increase the miscibility between CO_2 and water. The possibility of using absolute ethanol was analysed since the use of ethanol significantly enhances the solubility of water in scCO_2 [13], but also acetone, and methanol because of their affinity with both water and CO_2 . Moreover, the solubility of sodium bicarbonate in those three cosolvents is low: about 0.03 wt% in ethanol at 20 °C [14] (Table 2), in acetone (0.02 wt% at 22 °C and atmospheric pressure) [15], and in methanol (2.13 wt% at 22 °C and atmospheric pressure) [15].

Acetone was rapidly given up because of the following reasons: the

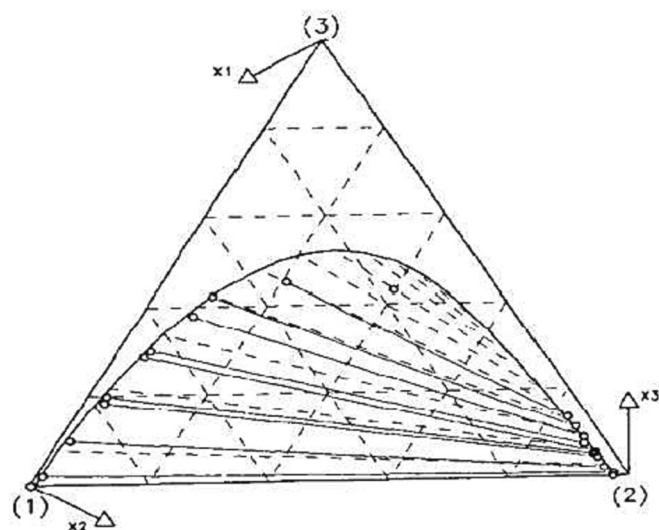


Fig. 3. Phase diagram of the system CO_2 /acetone/water at 40 °C under 100 bar [16] – CO_2 (1), water (2), acetone (3).

phase equilibrium diagram CO_2 /acetone/water (Fig. 3) [16] presents a rather narrow miscibility zone for mixtures rich in CO_2 (corresponding to an SAS process composition in the precipitation autoclave) and the minimum amount of acetone to add to water is 90:10 (mol%) which means 95:05 (wt%). The solubility of sodium bicarbonate in such a mixture of acetone:water 95:05 (wt%) remains very low [15] leading to a too small amount of sodium bicarbonate to process. Finally, acetone is not environmentally friendly.

Methanol had the features of a good candidate, validating both miscibility with water and CO_2 maintaining an acceptable solubility in the solution, but was given up for reasons of its toxicity.

Finally, ethanol was selected: it is a green solvent having a good affinity for both CO_2 and water, and even if sodium bicarbonate is weakly soluble in ethanol (Table 2), the amount of salt to be processed may be acceptable. The feasibility experiments were therefore performed using an ethanol:water solution of sodium bicarbonate.

3.1.2. Mass proportion of ethanol to use in the aqueous solution

The SAS process is efficient if the CO_2 /cosolvent/water mixture in the precipitation autoclave forms a single fluid phase under the operating conditions of pressure, temperature, and composition. The suitable mass proportion of ethanol:water to apply was deduced from the phase diagrams of the CO_2 /water/ethanol system.

To define the ethanol:water mass ratio to apply, the ternary system CO_2 /ethanol/water at 40 °C (Fig. 4) was considered [17]. The solubility curve of the system is broadly similar at 100 bar and 200 bar. During an SAS experiment, the precipitation autoclave is rich in CO_2 . In the CO_2 -rich region of the phase diagram (Fig. 4), it appears that the monophasic zone is narrow, leading to a small working area. To ensure a monophasic system when ethanol and water are mixed in a high amount of CO_2 , it is necessary to have an ethanol:water mixture rich in ethanol, at least at a molar ratio of about 80:20, which means about 90:10 in mass ratio. Whatever the operating conditions of pressure and temperature of the SAS experiments performed, no sodium bicarbonate powder could be

Table 2

Solubility of sodium bicarbonate in mixtures of ethanol: water in mass proportion under atmospheric pressure [14].

Temperature (°C)	Solubility range ((g·kg _{solvent}) ⁻¹) in					
	Pure ethanol	90:10 (ethanol:water)	70:30 (ethanol:water)	50:50 (ethanol:water)	30:70 (ethanol:water)	10:90 (ethanol:water)
20	0.0–0.3	1.5–2.0	6.0–6.6	12.0–14.1	18.8–12.0	68.5–70.9
40	0.5–0.8	2.0–2.3	7.7–8.1	22.0–23.1	40.6–41.7	94.6–94.8
60	0.7–0.9	2.5–2.6	10.2–10.8	33.3–35.7	67.0–68.2	126.2–126.8

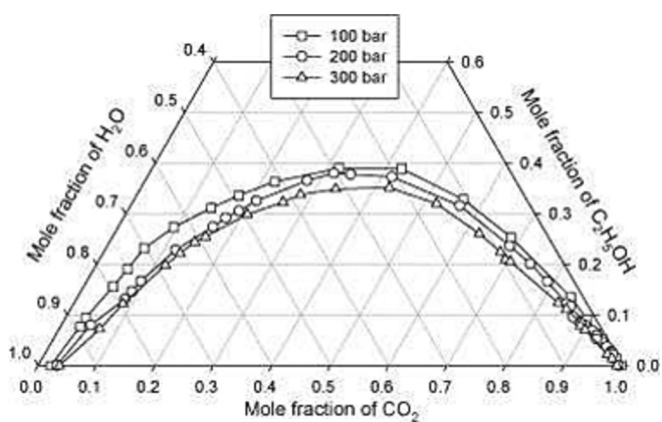


Fig. 4. Phase diagram of the system CO₂/ethanol/water at 40 °C, under 100 bar, 200 bar and 300 bar. [17].

recovered with an ethanol:water mass ratio lower than 90:10.

3.1.3. Precipitation of sodium bicarbonate using the SAS process

Table 3 gives the operating conditions studied for the precipitation of sodium bicarbonate from a solution ethanol:water 90:10 in mass ratio. All the experiments were performed using distilled water.

At this step of the study, the temperature and pressure were set at 40 °C and 150 bar, respectively. Those conditions ensure a good miscibility of the mixture CO₂/ethanol/water (Fig. 4) and are conventionally applied for the precipitation of solutes from aqueous solutions using the SAS process [18].

C° is the concentration of sodium bicarbonate in the aqueous solution. It is worth noting that the increase in the ethanol content of the solution leads to a far lower solubility of the sodium bicarbonate (Table 2) thus limiting the concentration C°. Three different concentrations of sodium bicarbonate were tested 0.3, 0.6 and 0.9 g·(kg_{solvent})⁻¹, taking care not to be too close to the saturation concentration.

The critical atomization jet velocity of ethanol in supercritical CO₂ is about 0.4 m·s⁻¹ between 90 and 110 bar at 313 K [19] while that of water is about 3.5 m·s⁻¹ at 90 bar; which presumably means lower at 150 bar [20]. One can expect the atomization velocity of the mixture ethanol:water to be intermediate to 0.4 and 3.5 m·s⁻¹ so that an atomization velocity of 2.6 m·s⁻¹ was tried corresponding to a solution flow rate of 2.0 mL·min⁻¹. To ensure such velocity, the capillary used had a 127 μm internal diameter.

Another important parameter is X, the ratio between the CO₂ mass flow rate and the solution mass flow rate. A high ratio may guarantee an efficient elimination of the solvent from the autoclave. The mass ratio X was varied from 15.4 to 21.6 (the corresponding CO₂ and solution flow rates are indicated in Table 3).

Experiment 1 allowed to precipitate a small amount of powder. The main amount of ethanol:water mixture was recovered in the solvent trap. However, the precipitated powder seemed to be slightly wet which means that the operating conditions chosen (injection velocity of 2.6 m·s⁻¹ and a mass ratio X of 15.4) allowed to effectively eliminate the

cosolvent and most of the water, however the solvent removal must be improved.

Experiment 2 was performed at the same operating conditions as experiment 1 except for the solution concentration that was lower (0.6 g·(kg_{solvent})⁻¹ against 0.9 g·(kg_{solvent})⁻¹ in experiment 1). The small amount of recovered powder through experiment 2 looked dry and all the ethanol:water mixture was collected in the solvent trap.

Finally, experiment 3 with a lower concentration (0.3 g·(kg_{solvent})⁻¹) and a higher CO₂ flowrate (leading to a higher X ratio) allowed the precipitation of a significant amount of dried powder (Fig. 5). It is important to highlight that the powder was very expanded since only 70 mg of sodium bicarbonate were precipitated and occupied a volume of about 60 cm³.

For this successful assay, the operating conditions were a pressure of 150 bar, a temperature of 40 °C, an injection velocity of 2.6 m·s⁻¹ and a mass ratio X of 21.6. The concentration of the sodium bicarbonate solution was voluntarily decreased to 0.3 g·(kg_{solvent})⁻¹. Indeed, the former experiments were performed using more concentrated solutions (0.6–0.9) g·(kg_{solvent})⁻¹, and at these concentrations, a white deposit (possibly lime) appeared after a certain time in the solution. This deposit systematically appeared for concentrations greater than 0.45 g·(kg_{solvent})⁻¹.

After the experiment, the content of the solvent trap was evaporated. No further traces of sodium bicarbonate were found. The precipitation yield for experiment 3 was then considered as high as 100%.

The powder sample was analysed by Raman spectroscopy to ensure that only the sodium bicarbonate solid phase was precipitated and did not contain any degradation compounds. Fig. 6 shows the Raman



Fig. 5. Powder obtained with experiment 3 performed at 150 bar, 40 °C, u = 2.6 m·s⁻¹, X = 21.6 (mass ratio), and C° = 0.3 g·(kg_{solvent})⁻¹.

Table 3

Operating conditions and corresponding results for a hydroalcoholic solution of sodium bicarbonate containing a mass proportion of ethanol:water 90:10.

Exp n°	Q _{solution} (mL·min ⁻¹)	u (m·s ⁻¹)	Q _{CO2} (g·min ⁻¹)	X (Q _{CO2} /Q _{solution}) (mol) / (mass)	C° (g·(kg _{solvent}) ⁻¹)	Result of the precipitation
1	2.0	2.6	25	63.3 / 15.4	0.90	Low amount of wet powder
2	2.0	2.6	25	63.3 / 15.4	0.60	Low amount of dry powder
3	2.0	2.6	35	87.8 / 21.6	0.30	Dry expanded powder
4	2.0	2.6	35	87.8 / 21.6	0.32	Dry expanded powder
5*	2.5	3.3	40	80.5 / 19.8	0.32	No precipitation

* Experiment performed with technical ethanol (purity 96%).

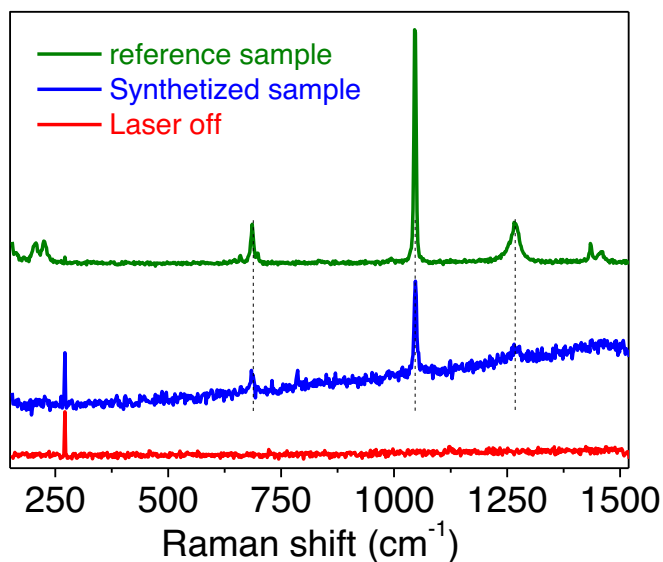


Fig. 6. Raman spectra of the reference sample in green and the precipitated powder from experiment 3 in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spectrum for the powder precipitated during experiment 3 compared to the sodium bicarbonate powder previously provided by the company Solvay before processing (so called reference sample). Through Table 1, the expected sodium bicarbonate solid phase occurs at the Raman shifts of 1046 cm^{-1} and 1268 cm^{-1} . On Fig. 6, the reference sample before processing is well characterized by two peaks at 1046 cm^{-1} and 1268 cm^{-1} . The powder precipitated by the SAS process shows a similar spectrum with the same Raman shifts. This confirms that the sodium bicarbonate powder precipitated by SAS was not degraded.

The powder is constituted of sodium bicarbonate crystals with a homogeneous polymorphism and an acicular habit. Some of the needles are very long with a $30\text{ }\mu\text{m}$ length. From the SEM observations, their width or equivalent diameter appears to measure between 300 and 500 nm (Fig. 7).

Repeatability of experiments was checked through experiments 3 and 4 which were conducted at the same operating conditions and led to the same results in terms of amount of precipitated powder, shape and size of the sodium bicarbonate crystals.

Finally, experiment 5 was conducted using technical ethanol (96%) instead of absolute ethanol (99.8%) in order to evaluate the influence of the cosolvent quality (Table 3). The mass ratio ethanol:water was maintained at 90:10 (ethanol:water). This assay could not lead to any precipitation of powder probably because during the steady-state installation and the solvent removing step, the use of technical ethanol instead of absolute ethanol could enrich the continuous phase in water, leading then to the resolubilization of the precipitated powder. This means that the slightest presence of humidity could be prohibitive for the micronization of sodium bicarbonate.

Through those first experiments, an efficient precipitation of sodium bicarbonate from a hydroalcoholic solution was possible at 150 bar and $40\text{ }^\circ\text{C}$ with a solution injection velocity of $2.6\text{ m}\cdot\text{s}^{-1}$ and a mass flow rate ratio X of 21.6 . The injection velocity of $2.6\text{ m}\cdot\text{s}^{-1}$ appears then to be sufficient to atomize the ethanol:water solution through the capillary.

3.1.4. Conclusions about the feasibility tests

Absolute ethanol as cosolvent was selected to be mixed with the sodium bicarbonate aqueous solution in mass proportion 90:10 ethanol:water in order to ensure miscibility between CO_2 and water in the SAS autoclave. The first precipitation experiments validated the possibility of the recrystallization of sodium bicarbonate from a hydroalcoholic solution using an SAS process. They also highlighted that a solution velocity of $2.6\text{ m}\cdot\text{s}^{-1}$ in the capillary and a mass flow rate ratio X of at least 21.6 allowed an efficient precipitation of sodium bicarbonate. The obtained crystals were needle shaped which unfortunately renders difficult their use in any application. In the following section, an optimization of operating conditions is proposed, in view to obtain shorter needles or crystals with isometric habit.

3.2. Optimization of the SAS process for the precipitation of sodium bicarbonate from a hydroalcoholic solution

The former results were used as a reference for the optimization step. The aim of this study is to understand the influence of operating conditions on the size and shape of the precipitated particles with a view to obtain isometric crystals. Table 4 shows the operating conditions tested and the corresponding results in terms of precipitation.

For all the experiments, absolute ethanol was used as cosolvent in the mass proportion 90:10 ethanol:water. The varied operating conditions were temperature (40 – $50\text{ }^\circ\text{C}$), pressure (120 – 180) bar, sodium bicarbonate concentration in the solution (0.3 – $0.45\text{ g}\cdot\text{kg}_{\text{solution}}^{-1}$) and injection velocity (2.6 – $4.2\text{ m}\cdot\text{s}^{-1}$). To reach the velocity of $4.2\text{ m}\cdot\text{s}^{-1}$, it was

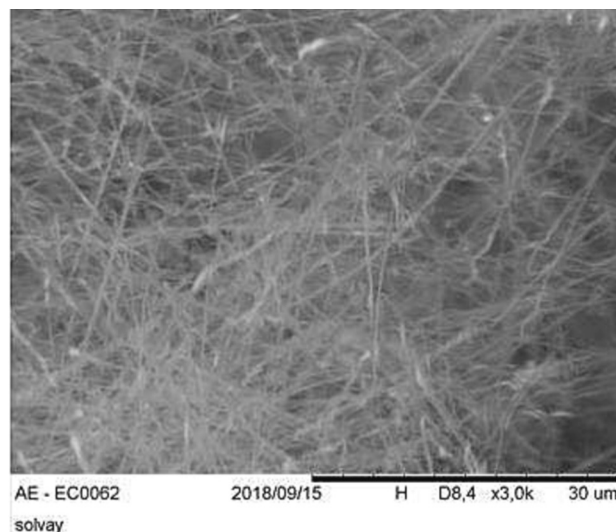
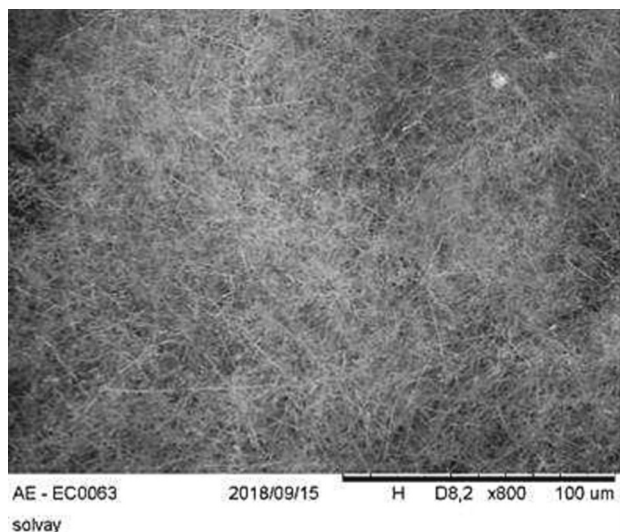


Fig. 7. SEM images obtained with powder precipitated from experiment 3 – magnitude $\times 800$ on the left and magnitude $\times 3000$ on the right.

Table 4

Sum up of operating conditions and corresponding results studied for the optimization of the recrystallization of sodium bicarbonate.

Exp n°	P (bar)	T (°C)	Capillary (µm)	Q _{alim} (mL·min ⁻¹)	u (m·s ⁻¹)	Q _{CO2} (g·min ⁻¹)	X (Q _{CO2} /Q _{alim}) (mol) / (mass)	C° (g·(kg _{solvent}) ⁻¹)	Result of the precipitation
4	150	40	127	2.0	2.6	35	87.8 / 21.6	0.32	Dry powder
6	150	50	127	2.0	2.6	35	87.8 / 21.6	0.32	Dry powder
7	150	40	100	2.0	4.2	40	101.6 / 24.7	0.29	Dry powder
8	150	50	100	2.0	4.2	40	101.6 / 24.7	0.29	Dry powder
9	120	40	127	2.0	2.6	35	87.8 / 21.6	0.32	No powder
10	120	50	100	2.0	4.2	40	101.6 / 24.7	0.30	Small amount of powder
11	180	50	100	2.0	4.2	40	101.6 / 24.7	0.30	Dry powder
12	150	50	100	2.0	4.2	40	101.6 / 24.7	0.45	Dry powder

necessary to decrease the size of the capillary to 100 µm. The influence of parameter X could not be studied because of limitations for the CO₂ flowrate delivered by the pump. However, the feasibility experiments highlighted that a mass ratio X at least of 21.6 guaranteed the solvent removal.

For all the assays, except for experiments 9 and 10, dry powder was obtained with a yield of 100% and Raman spectroscopy highlighted the targeted NaHCO₃ phase.

3.2.1. Influence of temperature

The experiments highlighting the influence of temperature on the sodium bicarbonate recrystallization are experiments 4, 6, 7, and 8 (Table 4).

To bring out the influence of temperature from 40 °C to 50 °C, this parameter was varied while maintaining all the other parameters constant.

For all the experiments, pressure was set at 150 bar but the atomization velocity, the mass flow rate ratio X and concentration were varied. It is possible to compare the experiments two by two:

- Experiments 4 (40 °C) and 6 (50 °C) were conducted with a sodium bicarbonate concentration equal to 0.32 g·(kg_{solvent})⁻¹ injected through a 127 µm internal diameter capillary, an injection velocity of 2.6 m·s⁻¹, and a mass flow rate ratio X of 21.6.
- Experiments 7 (40 °C) and 8 (50 °C) were performed with a sodium bicarbonate concentration equal to 0.29 g·(kg_{solvent})⁻¹ injected through a 100 µm internal diameter capillary which allowed an injection velocity of 4.2 m·s⁻¹. The mass flow rate ratio X was 24.7.

When comparing experiments 7 and 8 performed at 40 °C and at 50 °C, respectively, the temperature effect can be observed at macroscopic scale. Fig. 8 illustrates the influence of temperature on the difference of aspect of the obtained powders. Experiments realized at 40 °C led to expanded and homogeneous powders while those obtained at 50 °C were agglomerated in clusters, exhibiting a higher apparent density. Therefore, powders recovered at 50 °C were easier to handle. This behaviour was observed whatever the atomization velocity and solution concentration.

Raman spectroscopy once again confirmed the precipitation of the targeted NaHCO₃ phase which means that temperature from 40 °C to 50 °C did not degrade the product.

The SEM observations (Fig. 9a and b) show that for the operating conditions (2.6 m·s⁻¹ and concentration of 0.32 g·(kg_{solvent})⁻¹), an increase in temperature from 40 °C to 50 °C allowed to obtain needles or rather generally short sticks even if some sticks remain very long. Such observation is consistent with the powder aspect.

The comparison between the SEM photographs (Fig. 9c and d) obtained for injection velocities of 4.2 m·s⁻¹ did not reveal any influence of temperature in the crystal length. It can be suggested that at such atomization velocity, which is a high value regarding the atomization critical velocity of ethanol, the effect of atomization is preponderant over the effect of temperature.

3.2.2. Influence of pressure

The experiments that illustrate the effect of pressure on the sodium bicarbonate recrystallization are experiments 4, 8, 9, 10, and 11 (Table 4). Three pressures were studied: 120, 150, and 180 bar. The comparison was done at 40 °C and at 50 °C. All other parameters were



(a)



(b)

Fig. 8. Difference in aspect between powders precipitated at (a) 40 °C (experiment 7) and at (b) 50 °C (experiment 8).

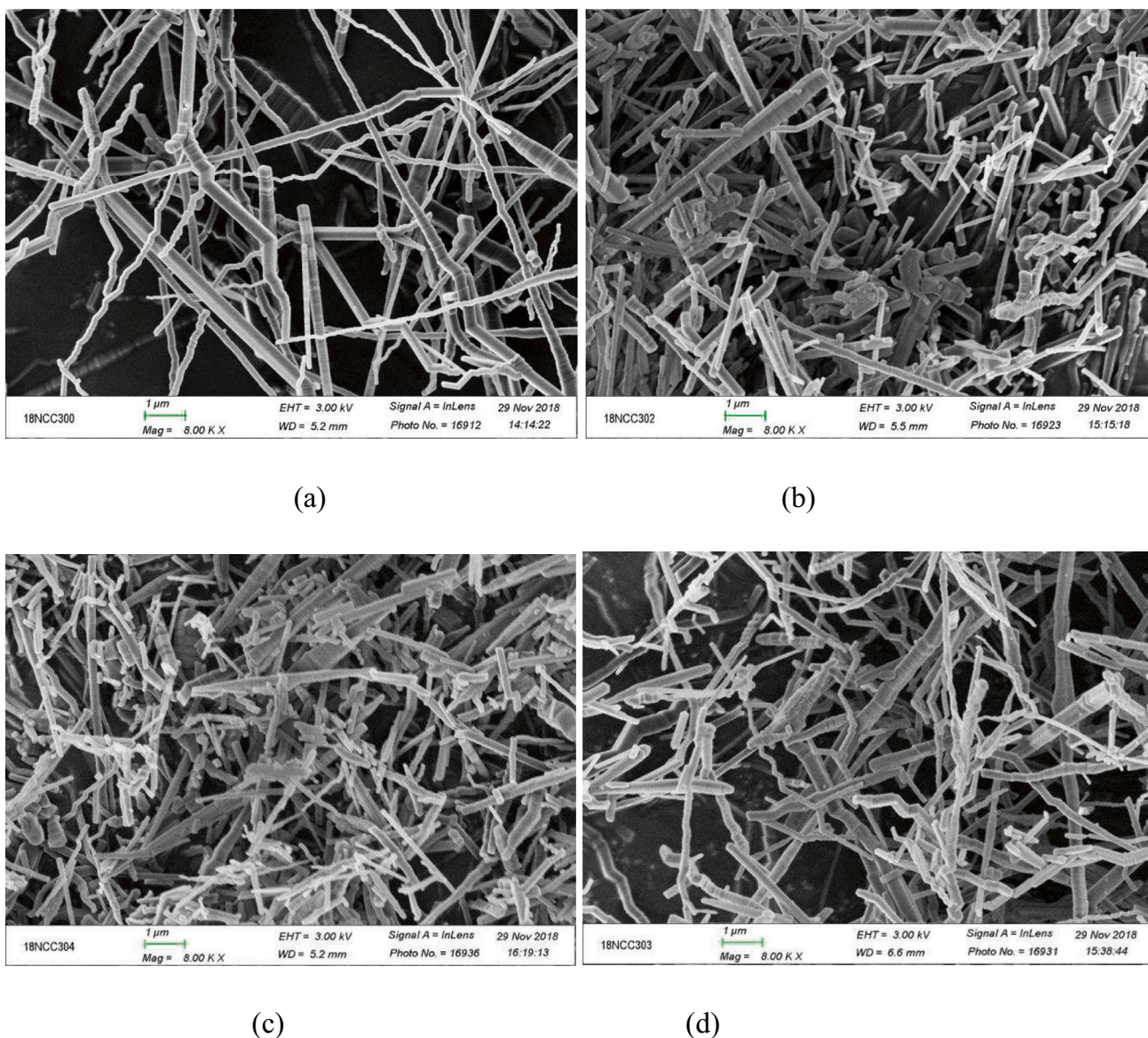


Fig. 9. SEM observations. Left column 40 °C and right column 50 °C. (a) Exp 4; (b) Exp 6; (c) Exp 7; (d) Exp 8.

chosen in order to ensure a good precipitation from the feasibility study (injection velocity at least $2.6 \text{ m}\cdot\text{s}^{-1}$ and mass ratio X at least 21.6).

Experiment 9 performed at 120 bar and 40 °C could not lead to the production of powder and experiment 10 performed at 120 bar, 50 °C led to very small amount of powder deposited on the wall of the autoclave. All experiments realized at higher pressures enabled the recovery of an expanded powder in the basket. This suggests that it is advisable to work at pressures at least equal to 150 bar to succeed in recrystallizing sodium bicarbonate from an ethanol:water solution.

Experiments 8 and 11, respectively carried out at 150 bar and 180 bar with all other parameters set constant allow to assess the influence of pressure on the produced crystal size. Fig. 10a and b compare SEM observations of powders obtained at 50 °C, respectively under 150 bar and 180 bar. The pressure seems not to have any significant effect on the crystal shape and size.

3.2.3. Influence of the concentration of the sodium bicarbonate solution

Experiments 8 and 12 bring to light the influence of concentration from respectively $0.29 \text{ g}\cdot(\text{kg}_{\text{solvent}})^{-1}$ to $0.45 \text{ g}\cdot(\text{kg}_{\text{solvent}})^{-1}$ on the sodium bicarbonate precipitation. As already described in section 3.1.2, it was not possible to study higher concentrations since above $0.45 \text{ g}\cdot(\text{kg}_{\text{solvent}})^{-1}$, far from the saturation concentration, a white solid (probably lime) appeared in the solution. Both experiments 8 and 12 were carried out at 150 bar and 50 °C with an injection velocity of $4.2 \text{ m}\cdot\text{s}^{-1}$, and a mass flow rate ratio X of 24.7. Fig. 11 compares SEM observations of the crystals obtained with the two experiments. An increase in concentration seems to lead to more homogeneous crystals in size. The sticks obtained with the highest concentration (b) look shorter but larger (300 nm) than with the lowest concentration (200 nm) (a). This result is obvious and consistent with what can be found in the literature [21]: higher concentration leads to higher supersaturation and higher nucleation frequency, shorter crystals can then be obtained.

Experiments 8 and 11, respectively carried out at 150 bar and 180 bar with all other parameters set constant allow to assess the influence of pressure on the produced crystal size. Fig. 10a and b compare SEM observations of powders obtained at 50 °C, respectively under 150 bar and 180 bar. The pressure seems not to have any significant effect on the crystal shape and size.

3.2.4. Influence of the injection velocity

It is expected that the injection velocity plays a preponderant role on recrystallization. This injection velocity should be higher than the critical atomization velocity.

In literature, the critical atomization velocity of ethanol is reported to be about $0.4 \text{ m}\cdot\text{s}^{-1}$ between 90 and 110 bar at 35–40 °C [19] and that of water about $3.5 \text{ m}\cdot\text{s}^{-1}$ at 90 bar [20]. All the experiments were performed at a velocity of at least $2.6 \text{ m}\cdot\text{s}^{-1}$, provided pressure and mass ratio X were at least 150 bar and 21.6, respectively, and allowed to

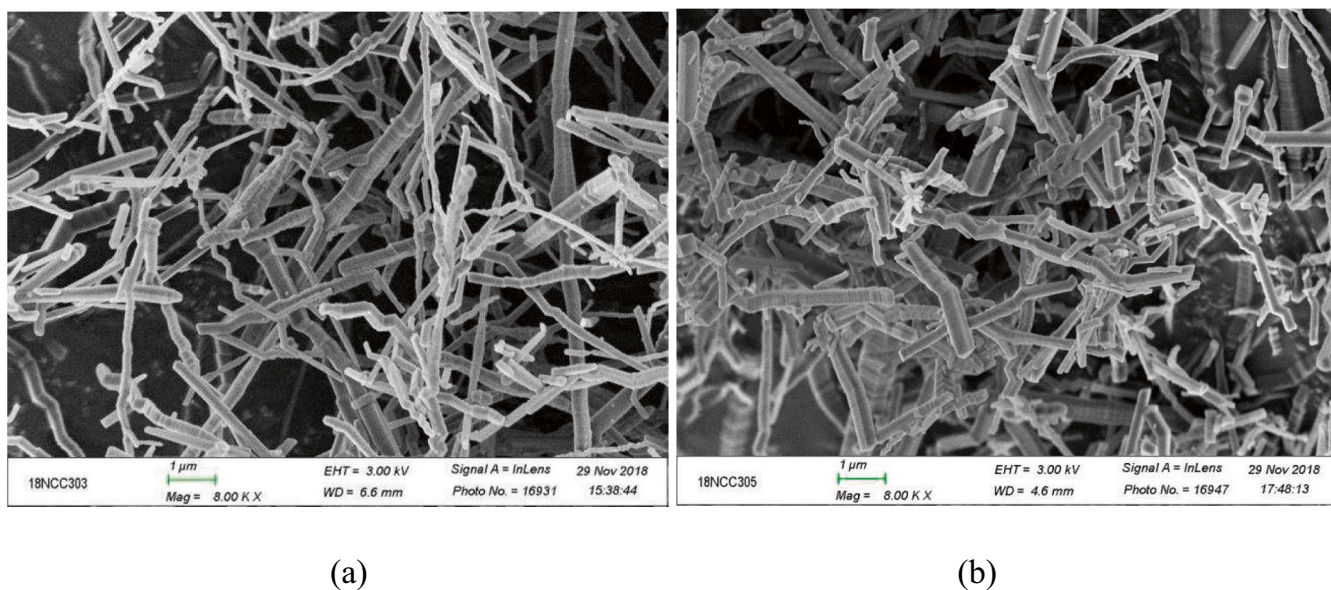


Fig. 10. SEM observations of recrystallized sodium bicarbonate at 50 °C under 150 bar (a) and 180 bar (b).

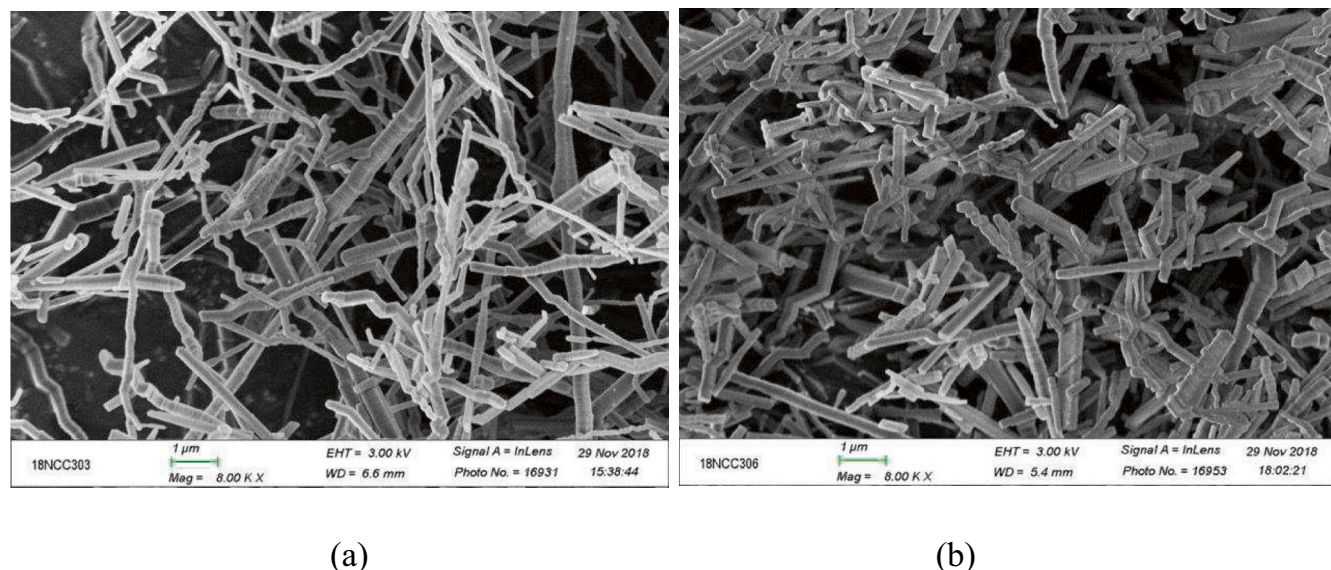


Fig. 11. SEM observations for crystals obtained for experiments realized with two different concentrations of the injected solution (a) Experiment 8 at $0.29 \text{ g} \cdot (\text{kg}_{\text{solvent}})^{-1}$ and (b) experiment 12 at $0.45 \text{ g} \cdot (\text{kg}_{\text{solvent}})^{-1}$.

obtain a fine powder of sodium bicarbonate crystals with acicular habit.

To change the acicular habit onto isometric shapes, higher injection velocities were tested; with a $100 \mu\text{m}$ capillary and a solution flow rate of $2 \text{ mL} \cdot \text{min}^{-1}$, it was possible to reach an atomization velocity of $4.2 \text{ m} \cdot \text{s}^{-1}$.

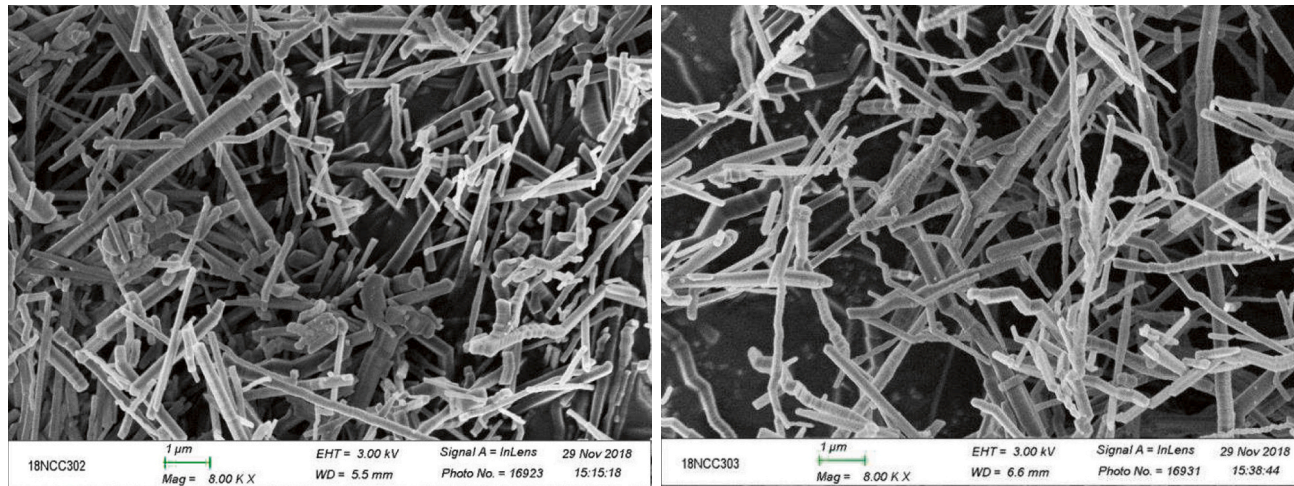
Fig. 12 shows SEM observations for two different injection velocities 2.6 and $4.2 \text{ m} \cdot \text{s}^{-1}$ (experiments 6 and 8, respectively).

Contrary to what was expected, the increase in the atomization velocity did not allow to modify the morphology of the particles. For the two velocities, sticks of a few micrometers in length and a few hundred nanometers in diameter were obtained. Increasing the speed therefore did not significantly improve the mixing conditions.

3.2.5. Mechanism of crystallization

SEM observations performed at high magnitude ($\times 30,000$) highlighted that the formed crystals consist of a succession of superimposed platelets (Fig. 13). Moreover, some sticks present a zigzag shape (Figs. 8 to 11).

Such a crystallization mechanism has already been observed and described by Oaki et al. [22]. The authors studied the growth of potassium sulphate (K_2SO_4) crystals in a polymeric solution of polyacrylic acid (PAA) at different concentrations. They obtained zigzag morphology crystals from concentrated PAA solutions. Two concomitant phenomena should be considered to explain the formation of such crystals. Firstly, adsorption (of a solute or in our case of a solvent molecule) on specific crystal faces can lead to the formation of tilted crystal units. In addition to the habit modification, a diffusion-limited condition may control the assembly of the tilted units. This zigzag shape could be the consequence of the association of twinned crystals, due to the variation of the diffusion conditions controlled by the solute concentration in the medium. Furthermore, Clercq et al. [23] proposed crystallization pathways commonly observed in the SAS process (Fig. 14). These authors found that Crystallization Particle Attachment (CPA) pathway can occur, either alone or together with classical growth mechanisms. From Fig. 14, the crystallization mechanism leading to sodium bicarbonate zigzag crystals obtained in this work using SAS



(a)

(b)

Fig. 12. Influence of the injection velocity at 150 bar, 50 °C – (a) 2.6 m·s⁻¹; (b) 4.2 m·s⁻¹.

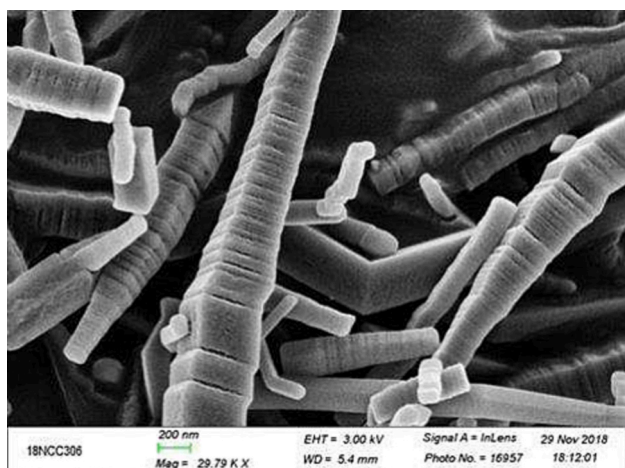


Fig. 13. SEM observation of a sodium bicarbonate crystal for a magni- tude $\times 29,790$.

experiments is probably the CPA pathway.

3.2.6. Conclusions

The purpose of this optimization study was to understand the in- fluence of operating parameters pressure, temperature, concentration of solution and atomization velocity on the size and morphology of crystals formed with a view to obtain isometric particles.

Whatever the operating conditions, the obtained crystals had a stick shape. Temperature varied from 40 to 50 °C and an increase in tem- perature seemed to lead to shorter sticks. Powders produced at 50 °C were easier to manipulate than the powders obtained at 40 °C. It was not possible to precipitate sodium bicarbonate at 120 bar. For pressures at least of 150 bar, no significant effect could be noticed on the produced particles. The solution concentration varied from 0.29 to 0.45 g·(kg_{solvent})⁻¹. The higher the concentration, the thicker the produced crystals. Finally, the studied atomization velocities were far higher than the critical atomization velocity of pure ethanol. An increase in the ve- locity did not have any significant influence on the crystal length. The variation of operating conditions in the studied field could not modify the morphology of the formed crystals. The observation of the crystals

under high magni- tude showed that the sticks are constituted of super- imposed platelets probably resulting from growth by CPA mechanism.

4. General conclusions

The aim of this study was to develop a sustainable single-step process involving scCO₂ to recrystallize sodium bicarbonate from an aqueous solution. As sodium bicarbonate is not soluble in scCO₂, the SAS process logically imposed itself.

The SAS process could lead efficiently to sodium bicarbonate recrystallization provided that absolute ethanol in the mass proportion 90:10 (ethanol:water) was added to the initial bicarbonate aqueous solution to render the solvent mixture miscible with scCO₂ whatever the operating conditions. It was also necessary to work under a pressure at least of 150 bar, an atomization velocity of at least 2.6 m·s⁻¹ and a mass flow rate ratio X of at least 21.6. The sodium bicarbonate crystals were in the shape of long and thin zigzag sticks which were difficult to handle. SEM observations showed that the sticks were constituted of super- imposed platelets potentially resulting from a CPA mechanism.

Some operating conditions were varied to try to render the shape of the crystals more isometric. The most favourable conditions leading to the thickest and shortest crystals in the studied experimental domain were a pressure of 150 bar, a temperature of 50 °C, an atomization ve- locity of 2.6 m·s⁻¹, and a solution concentration of 0.45 g·kg_{solvent}⁻¹. No significant influence of higher pressure and atomization velocity was noticed. An addition of additives / an additive could be considered in order to block the growth of the sticks during the SAS process and might lead to more isometric crystals. Even if it were not possible to obtain an isometric habit, this study was unquestionably successful in obtaining powders with new characteristics in terms of morphology and habit, opening up the field of possibilities for novel applications.

Credit author statement

The manuscript Powtech POWTEC-D-22-03032 untitled “Novel crystal morphology for sodium bicarbonate obtained by using the Supercritical Anti-Solvent Process” was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally. Project administration, resources, analysis, and validation:Thibaut Detoisien, Lama Itani and Frédéric Nicolas. Conceptualization, methodology, experiments,

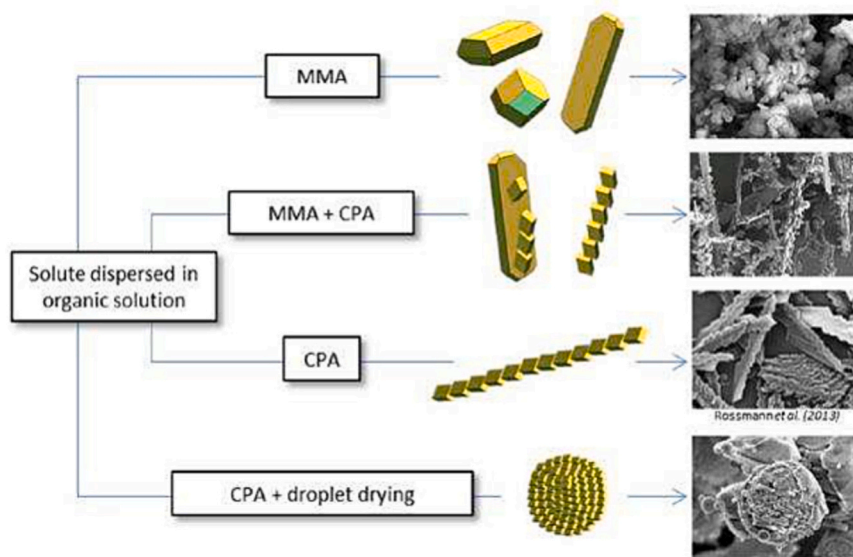


Fig. 14. Proposed crystallization pathways commonly observed in the SAS process. MMA: Monomer-by-Monomer Addition. CPA: Crystallization by Particle Attachment [23].

validation, and writing: Christelle Crampon, Emmanuelle Myotte and Elisabeth Badens.

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.

Data availability

No data was used for the research described in the article.

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