A SUPERCRITICAL PROCESS TO PRODUCE COCOA BUTTER AND CHOCOLATE PARTICLES FOR THE SEEDING OF CHOCOLATE

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A continuous and original process using supercritical CO_2 has been developed in our laboratory to produce cocoa butter and chocolate micro-particles. Depending on the operating conditions it is possible to obtain 100 % cocoa butter crystals in the suitable form V. In this process, liquid cocoa butter (or chocolate) is continuously introduced in an autoclave and mixed with a continuous flow of supercritical CO_2. This process can also be used with chocolate as the starting raw material.

With cocoa butter and under these conditions two fluid phases are present - one is rich in CO_2 (˜ 99%) and the other is rich in cocoa butter (˜ 70%). The temperature and pressure are chosen to have similarity of density between these two phases. The mixture is stirred to form an emulsion. The lower the density difference, the more stable the emulsion. Particles are obtained by spraying out this emulsion through a nozzle in another vessel at a lower pressure, which can be different from the atmospheric pressure.

These particles were characterised using differential scanning calorimetry (DSC), particle size distribution analysis and environmental scanning electron microscopy (ESEM). The polymorphism of the particles produced - form V - as well as their size and morphology allow them to be used to seed the chocolate in the tempering step of the chocolate manufacturing process.

INTRODUCTION

Chocolate is a mixture of two powders, grinded cocoa nibs and caster sugar, coated with fat. It is this fat, the cocoa butter, which is responsible for the nice feeling of eating chocolate. Indeed, the melting range of cocoa butter allows the chocolate to melt in the mouse but not at room temperature.

Cocoa butter, can crystallise in six different forms. The most desirable form is form V because of its stability and its melting temperature (32-34 °C, 306 K), which gives hardness and glossy aspect to the final product. In addition, less stable crystals (mainly form IV) may transform during storage to the more stable form V. This transition will be accompanied by a migration of large fat crystals to the surface giving an unpleasant grey aspect known as "chocolate bloom" [1].

Producing chocolate with cocoa butter directly in form V is therefore a major challenge in the chocolate industry since it prevents from the blooming of chocolate. To reach this goal the manufacturers have introduced in the process a tempering stage. Tempering is a pre-crystallisation step aimed at the formation of form V seed crystals, which in turn will force the remaining fat to crystallise in this stable form. Starting with hot liquid chocolate, tempering consists in a series of temperature changes to crystallise the fat, then to melt only the less stable crystals and finally seed the bulk with the remaining more stable crystals.

In a previous study, we have found that supercritical processes can be applied to cocoa butter in order to produce form V particles. The supercritically-produced particles can advantageously be used to seed the bulk of hot chocolate and therefore an alternative to the classical tempering step can be proposed [2].

In the work presented here, we have modified the process in order to have a continuous operating mode and we have extended the raw material used in order to use chocolate instead of cocoa butter.

I - MATERIALS AND METHODS

1.1 Experimental apparatus

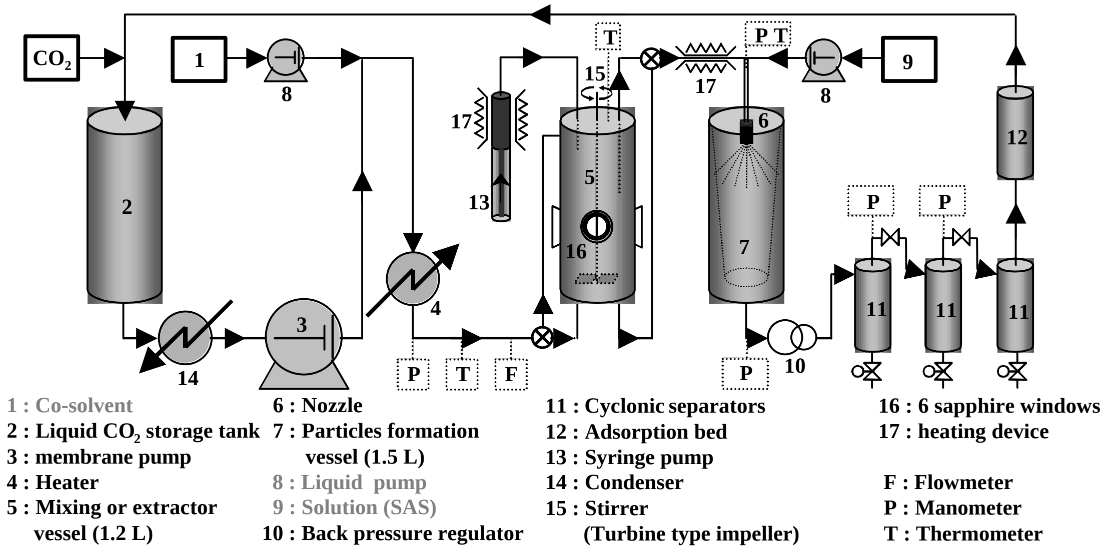

Figure 1: Scheme of the experimental device

The experiments were carried out in a versatile pilot plant (Separex, France). A schematic diagram of the apparatus is shown in figure 1. Carbon dioxide is cooled and stored in a liquid CO_2 storage tank (2). It can be circulated at a maximum flow of 30 $kg{\cdot}hr^{-1}$ by a membrane pump (Lewa, Germany) (3). Compressed CO_2 passes then through a heat exchanger (4) and becomes supercritical. Some of the devices (1, 8, 9) shown in figure 1 are used for other experiments such as SAS or RESS with co-solvent.

The vessel (5) (PARR Instrument, USA) is equipped with 6 sapphire windows (16), three of them placed at the bottom and the three others at middle height, a magnetic stirrer (15) with a maximum torque of 1.8 Nm and a flexible mantle heater. The flow coming out this vessel is sprayed into the expansion vessel (7) by means of a nozzle (6). The two following nozzles were used in this study:

- nozzle (1): Spraying System Spraydry SK-SIY80-SKY16, with an orifice insert diameter of 340 µm.
- nozzle (2): Top Industries coaxial tube, 3 cm long with an inlet diameter of 100 µm.

The powder formed is collected in a porous bag made of PTFE fibres. Then, CO_2 is depressurised (10) and can either be directed to the vent or purified and recycled.

1.2 Cocoa butter particle generation

In a previous work [2] we used a batch process to generate the cocoa butter particles: the cocoa butter was loaded into the vessel (5) and this vessel was fed with pure CO_2. Two fluid phases were present - one rich in CO_2 (˜ 99 %) and the other rich in cocoa butter (˜ 70 %) [3]. Two series of experiments were done, one with the tube between the vessel (5) and the nozzle fixed at the bottom of (5) and one with this tube fixed at the top of (5). For the first series of experiments the phase leaving (5) was too poor in cocoa butter leading to a very low production rate of particles. For the second series, the particles obtained had too wide a size distribution. In addition, in these two processes we observed that the particles composition evolved within a single experiment probably due to a fractionation phenomenon. For all these reasons we have chosen to adapt the experimental set-up to a continuous one.

This new process is semi continuous: CO_2 and melted cocoa butter are continuously introduced in the vessel (5) their flow rate being controlled during all the experiment. However, the collection of the particles in the bag of the vessel (7) is still in batch mode. To decrease the time required to obtain the steady state, pieces of cocoa butter are firstly loaded in the vessel (5) and their mass has been chosen to fit with the desired flow rate ratio of CO_2 vs cocoa butter. Then the vessel is filled with CO_2, heated and stirred until reaching equilibrium at the operating pressure and temperature. It can be noticed that the melting temperature of cocoa butter decreases under pressure of CO_2. In all experiments, the quantity of cocoa butter is far over the theoretical quantity solubilised in a saturated phase of supercritical CO_2. Therefore, two fluid phases are present and each of them is assumed to be saturated.

Once a stable temperature has been reached, the valve between both autoclaves (5) and (7) is then opened simultaneously with the flow of CO_2 coming from (4) and the flow of melted cocoa butter coming from (13). This melted cocoa butter is introduced continuously into the vessel (5) by means of a syringe pump (Isco 260 D) with a controlled flow rate.

1.3 Chocolate particle generation

The black chocolate used for these experiments is made of cocoa (86 %), sugar and lecithin. After stirring the mixture it was impossible to see the emulsion stability through the sapphire windows for the rest of the experiment. We used the best operating conditions observed with cocoa butter without being sure that the emulsion was stable. The presence of solid particles of sugar and grinded cocoa liquor has to be considered. We made the assumption that this suspension does not sediment since

- these particles are small ($< 30\ \mu m$),
- the two fluid phases have nearly the same density
- the mixture is strongly stirred.

1.4 Powder characterisation

Differential scanning calorimetry (DSC) has been used to characterize the samples in a DSC-7 Perkin-Elmer. The DSC patterns of the samples (2-5 mg) were obtained between 283 K and 323 K at a heating rate of $5\ K \cdot min^{-1}$ in a N_2 gas stream. Since the samples are kept in a refrigerator, some of them have been characterized again after 3 weeks in order to test their shelf stability.

In order to use these powders for chocolate seeding, a characterisation of their mechanical and rheological properties is needed. A particle size distribution analysis was made using a TSI aerosizer model PSD 3603 and the apparent density was measured for each sample obtained.

Pictures such as those presented in figures 2 and 3 have been made with an Environmental Scanning Electron Microscope (XL30 ESEM FEG, FEI Philips, Netherlands).

II- RESULTS AND DISCUSSION

The properties of the emulsion made between the two fluid phases by stirring depend on three main operating conditions: the pressure, the temperature and the mass ratio of CO_2 vs cocoa butter. More precisely the key parameter is the density of the CO_2 richest phase. The behaviour of this unstable emulsion is crucial in the process. In fact, if the emulsion is not stable, that is if it takes a very short time for the two phases to separate, a light one and a heavy one, the composition of the flow feeding the nozzle (6) will change during the experiment.

As an example, the operating conditions in the vessel (5) were the following: 15 MPa, 343 K. The flow rate ratio of CO_2 vs cocoa butter was fixed to 3.8, so the vessel has been initially loaded with 250 mL of melted cocoa butter (total volume = 1.2 L). CO_2 at 7.9 kg·hr^{-1} and liquid cocoa butter at 2 kg·hr^{-1} are continuously introduced, the mixture is stirred and the tube (1/4 " OD) leading to the nozzle is fixed on the top of vessel (5). The two phases separates upstream the nozzle and most of the heaviest one falls back into (5). This can be explained by the large difference between the densities of the separated phases and because the maximum global flow rate is low (30 kg·hr^{-1}).

Several trials were made to test how long is this emulsion stable. The criterion was the time it took to see that 90 % of the mixture is homogeneous after having stopped the stirrer. The best result i.e. the longer time was obtained at 26.5 MPa and 306 K. At this point there is an inversion of the density of each phase: the richest in cocoa butter becomes the lighter when increasing the pressure or decreasing the temperature. Under these conditions the density of pure CO_2 is 0.95 and the same phenomenon might probably be observed all along this isochore but could been studied because the maximum operating pressure in (5) is 30 MPa.

Since the operating conditions ensured that the emulsion was stable it did not matter whether the connection between the vessel (5) and the nozzle starts at the bottom or at the top of the autoclave. Provided these conditions can be kept during all the experiment it was admitted that the composition of the mixture remained unchanged. At the maximum flow rate of the pump (3) (30 kg·hr^{-1}), the ΔP provoked by the nozzle (1) (340 μm) is just sufficient to keep the pressure at 26 MPa for the generation of cocoa butter particles. With the nozzle (2) (100 μm) it is easier to control all the parameters since the operating pure CO_2 flow rate average value is 7 kg·hr^{-1}. With this value the residence time into and upstream the vessel (5) is longer, so there are less temperature fluctuations, and consequently the process is easier to control.

Most of the samples obtained with pure cocoa butter are in form V with sometimes a minor part in form IV. Because the melting point of the form IV is close to that of the form V, a small quantity of form IV can change the slope of the onset point. That is why the common main criteria used to compare DSC patterns is the peak temperature and the specific heat. The average peak temperature of the samples obtained with pure cocoa butter is 304.5 K (31.4°C). DSC patterns of similar samples have been presented in [2].

The main results are the following:

• there is no influence of the process (batch or continuous, type of nozzle) on polymorphism

• the presence of form IV is uncommon and has only been detected when the pressure in the vessel (5) is “low”: $P_5 < 12$ MPa or when the temperature in the vessel is “high”: $T_5 > 333$ K (60°C) or also when the pressure in the expansion vessel (7) is kept high: P7 > 5 MPa. The common point of these experiments is the vessel temperature which is high comparing to other experiments.

The particle size distribution analyses were reproducible and the two major parameters are the nozzle and the ΔP. For a given flow rate through the nozzle the pressure P_5 is higher with the nozzle (1) and the particles are slightly finer. For the following experiment: global flow rate=27 kg·hr^{-1} with a ratio of CO_2 vs butter of 10, T_5=298 K, P_7=2 MPa, the particle size distribution analyses are (length unit=μm):

Nozzle	P_5 (MPa)	Mean diameter	Median	D 4,3	D 3,2
1	155	0.895	1.02	34.8	5.94
2	253	1.16	1.76	27.5	8.49

The apparent density value varies from 0.04 g·ml^{-1} to 0.31 g·ml^{-1}, the lightest powders being more often obtained with the nozzle (2).

A typical particle shape obtained with ESEM is shown in figure 2. It looks like a big agglomerate of smaller ones.

With chocolate, the emulsion is more viscous: when comparing two similar experiments the first with cocoa butter and the second with chocolate, we noticed that the rotation speed of the stirrer was lower with chocolate. This is why it is possible to use the larger nozzle (1) with a flow rate low enough to control the process. The advantage in using this nozzle concerns the width of the particle size distribution which is finer compared with the capillary.

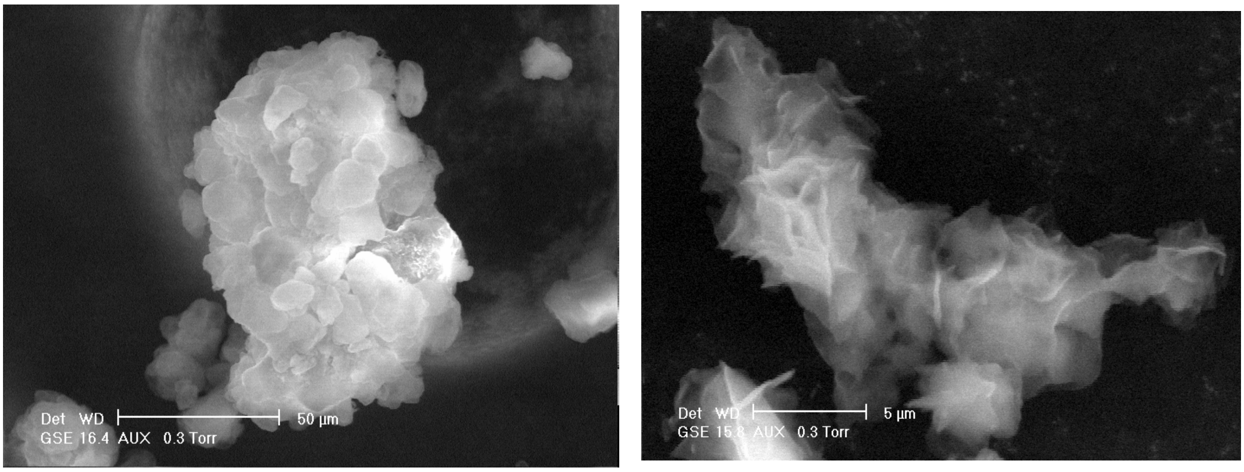

Figure 2: ESEM picture of a cocoa butter particle (left) and chocolate particle (right)

A typical DSC pattern for a chocolate experiment and the corresponding particle size distribution is presented in figure 3. These particles were obtained with the following operating conditions: P_5 = 26 MPa T_5 = 312K global flow rate 27 kg·hr^{-1} with a ratio at 5, nozzle (2). Its apparent density is 0.18 g·ml^{-1}. Its characteristic are in μm: Mean diameter = 1.57; Median = 1.68; $D_{4,3}$ = 13.6; $D_{3,2}$ = 7.01; specific surface area = 0.856 m^2·g^{-1}.

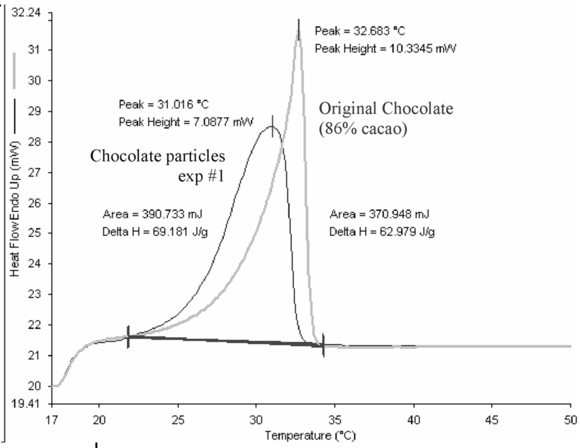

Figure 3 : DSC pattern and particle size distribution for chocolate particles

CONCLUSION

A continuous process to produce chocolate particles has been presented. The main objectives which were to obtain fine (max. diameter=30µm) and morphological form V particles is fulfilled. This has been possible by choosing the operating conditions to have an emulsion of two fluid phases in equilibrium at almost the same density. These operating conditions have been set up with pure cocoa butter and then applied to chocolate.

Seeding with these chocolate particles has not yet been done and will have to be compared with previous works [4]. Cocoa butter particles supercritically generated have already been tested to seed chocolate [2] and the results were of major interest especially concerning the temperature at which the seeding could been carried out (305 K). With chocolate particles we would hope even better results. The fine characterization of the chocolate powder (flowability, etc.) is under way.

In the view of an industrial application this process could possibly be adapted to spray the particles directly into the liquid chocolate during the tempering step as explained in [5].

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