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Physicochemical characterisation of the lactoperoxidase system powders: comparison of two drying techniques

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Abstract

A good knowledge of powder flow properties is necessary to consider industrial application of a system. Flowability is a complex combination of different parameters like size, shape or surface properties of particles. The goal of this study is to compare the impact of two drying techniques (freeze-drying and spray drying) on powder flowability in order to choose the most appropriate device. Powder is first studied at the particle level with size measurements and shape description. Then, the global behaviour is characterised by water content, water up-take and physicochemical analysis. Finally, the influences of two additives and of coating on powder flow properties have been investigated. The two powders obtained by spray and freeze-drying vary principally by the shape of the particles. Residual water content, moisturising capacity and surface properties are similar. In both cases, powder flowability is bad. Results obtained with the two additives show no improvement of powder flow properties. However, coating reduces the number of fine particles and, as a consequence, improves powder flowability with furthering particle motion.

Keywords: Flow property; Powder characterisation; Drying methods; Lactoperoxidase

1. Introduction

The most important property of a powder in food industry is its microbial stability, but end-use properties such as flowability or handling ability are very important too. In this work, two drying techniques have been tested and physicochemical properties of the obtained powders are examined in order to determine the most adapted process for food industry application. The lactoperoxidase system (LPS) has been chosen as model. This system is composed of lactoperoxidase (LPO, EC 1.11.1.7), which is a basic glycoprotein present in mammalian secretions like tears, milk or saliva, and thiocyanate (SCN^-). This system allows thiocyanate (SCN^-) conversion into hypothiocyanite ($OSCN^-$) with H_2O_2. Hypothiocyanite is a very powerful antibacterial agent. It binds on SH groups of bacterial proteins, which leads to reversible inhibition of most Gram-positive bacteria such as *Listeria monocytogenes*, and to irreversible inhibition of Gram-negative bacteria like *Escherichia coli* [1]. To be activated, the system needs hydrogen peroxide. In natural conditions, some *Lactobacillus*, *Lactococcus* or *Streptococcus* [2] can produce H_2O_2 under aerobic conditions. In our work, the lactoperoxidase system is activated artificially with an enzymatic generator, an association of glucose oxidase (GOD) and glucose (Fig. 1).

Interest of using enzymatic generation instead of direct addition is the increase of antibacterial activity by progressive liberation of hydrogen peroxide [3]. From the

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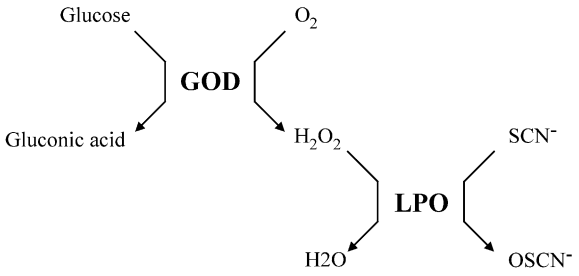

Fig. 1. Global reaction of hypothiocyanite production by lactoperoxidase system coupled with enzymatic generation of hydrogen peroxide.

perspective of encapsulation of the LPS and its hydrogen peroxide generator, a dry core containing both enzyme substrates (glucose and thiocyanate) has been produced. Due to the sticky behaviour of glucose and the hygroscopicity of thiocyanate, an inert polymer has been added to stabilise the mixture. Acacia gum has been chosen for its ability to control water uptake and its low viscosity at high concentrations allowing good drying rate [4]. Cores containing glucose, thiocyanate and acacia gum have been made using two processes: freeze-drying and spray drying. Spray drying is a simple and low cost method easy to extrapolate in industry. Freeze-drying is more difficult to transpose and six times more expensive, but is very respectful of the product. It also implicates a second step of grinding in order to calibrate final size of the particles.

In a previous work, the antimicrobial activity of the lactoperoxidase system using encapsulated substrates has been studied [5]. In this paper, we propose to focus on physical behaviour of the dry cores obtained by both methods in order to characterise the behaviour of the formed powder and to choose the most appropriate device for an industrial application. After a morphological study by microscopy and image analysis of the particles, physicochemical properties and global behaviour of powders are determined.

Table 1
Water activity of salts at 20 °C [8]

Salts	LiCl	$MgCl_2$	NaBr	$CuCl_2$	KI	$SiCl_2$
A_w	0.11	0.33	0.58	0.68	0.69	0.71
Salts	NaCl	NH_4Cl	KCl	$BaCl_2$	KNO_3	K_2SO_4
A_w	0.75	0.77	0.84	0.90	0.95	0.97

2. Materials and methods

2.1. Core production

Freeze-drying and spray drying powders have the same composition: D-glucose (Sigma, France) 40 g/l, potassium thiocyanate (Labosi, France) 8 g/l and acacia gum (Colloids Natural International, France) 100 g/l.

Aliquots of 10 ml were frozen at −30 °C and freeze-dried for 2 days with a Lyovac GT2E machine (Amsco/Finnaqua) at 2 bars and −45 °C. Then, freeze-dried block was ground with a bead grinder Retsch using one steel bead (∅: 6 mm, weight: 2 g).

Spray-dried powder was obtained on a Niro Atomizer Minor with an inlet air temperature of 170 °C, an outlet of 90 °C, a rotary nozzle and a product flow of 5 Hz (pump motor frequency).

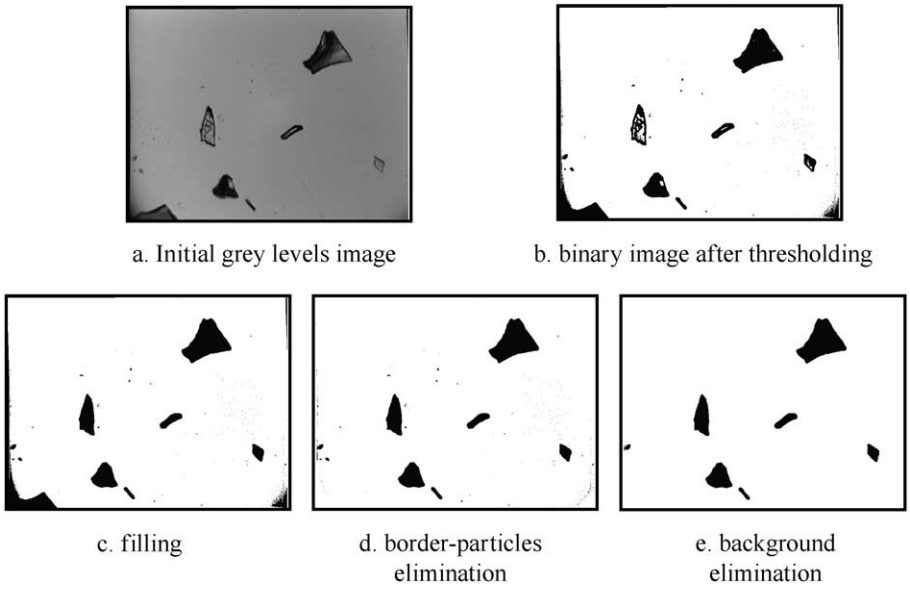

Fig. 2. Different steps of image analysis: (a) crude picture, (b) after thresholding, (c) after filling, (d) after border particles elimination, (e) after background elimination for freeze-dried powder.

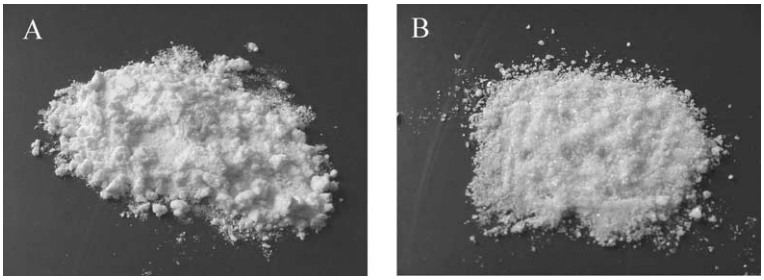

Fig. 3. Macroscopic observation of (A) spray drying powder and (B) freeze-drying powder.

2.2. Single particle analysis

Particles were observed by scanning electronic microscopy (JEOL JSM T330 A). Samples were placed on a brass cylinder and coated with a gold palladium thin layer with a Fine-Coat Ion Sputter JFC 1100.

Morphological analysis was performed by automated image analysis using routines developed within a commercial package (Visilog 5, Noésis, Les Ulis, France). The particles were observed by optical microscopy (Leitz Dialux 20) fitted with a CCD monochrome camera connected to a MATROX grabbing board. The initial grey level image (256 grey levels) was automatically segmented (threshold selection based on the examination of the histogram entropy) [6]. The obtained binary image was improved by shape filling, elimination of particles in contact with the image frame and background noise elimination (Fig. 2). The size and shape descriptors characterising each particle (in fact, its silhouette) were calculated on this final binary image.

Size is assessed by:

- the projected equivalent diameter: $D_{eq} = 2\sqrt{S/\pi}$ where S is the silhouette surface
- the Feret minimal diameter (F_{min}) and the Feret maximal diameter (F_{max}), which characterise the silhouette breadth and length.

From those size descriptors, two morphological descriptors were calculated: the circularity defined as: $C = P_c^2/(4\pi S)$, where P_c is the Crofton perimeter b [6], and two elongation factors, F_{max}/F_{min} and F_{max}/D_{eq}.

Two mesoscopic descriptors were finally computed: robustness, related to the elongation of the particle (when F_{max}/F_{min} is related in fact to the elongation of the silhouette convex bounding polygon) and the largest concavity index [7].

At the end, the size distribution of each type of particle is studied by laser diffraction with a Malvern Mastersizer S (Malvern Instruments) in wet basis. Particles are suspended in ethanol and observation is performed with 300RF lens which allows size measurements between 0.05 and 900 μm. Results obtained are diameters of equivalent spheres expressed in volume. The value d_{10}, d_{50} and d_{90} are notified, and those values mean that 10%, 50% or 90% of particles have a diameter lower than this value. Size of the distribution is also calculated: span=$(d_{90} - d_{10})/d_{50}$.

2.3. Powder characterisation

Residual water content of the two powders was determined and compared to the initial product humidity. One gram of freeze-dried powder, spray-dried powder, glucose, thiocyanate and acacia gum were placed in an oven at 110 °C for 12 h. Residual water content was calculated from the difference of weight before and after drying. Each test is carried out in triplicate.

Water sorption isotherms of all components were obtained by microclimate method. One gram of product

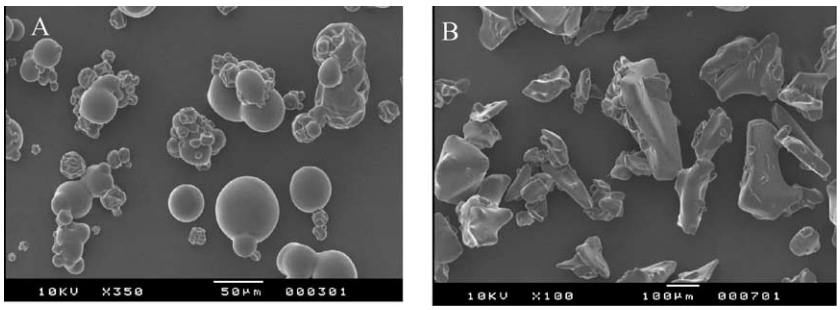

Fig. 4. Scanning microscopic observation of powders obtained by (A) spray drying and (B) freeze-drying.

Table 2
Shape descriptors calculated by image processing

	Circularity	F_{max}/F_{min}	F_{max}/D_{eq}	Robustness	Largest concavity index
Spray drying					
Mean	1.072	1.192	1.103	0.802	0.029
Standard deviation	0.217	0.230	0.112	0.077	0.064
Freeze-drying					
Mean	1.926	1.825	1.460	0.666	0.115
Standard deviation	2.188	0.702	0.329	0.139	0.127
Disk	1	1	1	0.8	0

was placed in sealed jar containing a salt-saturated solution [8] with a known water activity (A_w) (Table 1). After 3 weeks at 20 °C, product was weighted and results were treated with Water Analyser Series 2.05 software [9].

The powder physical properties were evaluated with a Hosokawa Micron Powder Tester PT-R. The powder compressibility was calculated from apparent aerated and apparent tapped densities, flowability from angle of repose and angle of fall values and floodability from the difference between the two above angles [10].

Surface chemical characterisation was done using Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy. Infrared spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (BRUKER IFS 55) connected to a diffuse reflectance device (Harrick). Detector was of the MCT type and cooled at liquid nitrogen temperature. Resolution was fixed equal to 2 cm^{-1}. Sample was gently ground and diluted in nonabsorbent KBr matrix (70 mg of sample/370 mg of KBr). Optical line was adjusted to avoid contribution of specular reflection. All diffuse infrared spectra are shown in absorbency units (log R_{KBr}/R_{sample}, where R is the intensity of the diffused part).

3. Results and discussion

3.1. Preliminary observations

The morphology of the powder differs depending upon the drying process. Macroscopic observation shows some size, texture and colour differences (Fig. 3). Freeze-dried powder seems to have a crystalline structure, and its flowability properties are better than those of spray-dried powder which tends to be more cohesive.

Scanning microscopy reveals shape difference (Fig. 4). Freeze-drying leads to angular particles with low sphericity, while spray drying gives rounded particles. Some small particles of the spray-dried powder are adsorbed on the surface of larger ones due to high surface particle interactions. To better characterise both types of particles and to confirm those observations, an image processing study is realised.

3.2. Quantitative morphological characterisation

All results are compared to a disk that is characterised by circularity and elongation factors (F_{max}/F_{min} and F_{max}/D_{eq}) equal to 1.

Spray-dried particles are round with a circularity close to 1. Particles are convex as shown by the very low concavity (Table 2). Freeze-drying leads to more angular particles. Circularity is equal to 1.9 revealing particles that departs from a disk, either because of their roughness and/or their elongation. The elongation factors are larger than 1, robustness is low and largest concavity index is high, revealing the high level of irregularity of the particles. The standard deviation of each descriptor is large, translating the important heterogeneity of the freeze-dried population.

3.3. Size distribution

The final freeze-dried powder is obtained after grinding. Different grinding times have been tested between 10 and 60 s. Results are presented in Fig. 5.

The increase of the grinding time decreases the size of the freeze-dried particles (Fig. 5), but it is directly correlated with a large increase of the distribution span. With this grinding method, it is difficult to obtain a particle size smaller than 100 μm. The wide distribution observed after 60 s of grinding is linked to agglomeration phenomena due to heating inside the vial (Fig. 5). According to those results, a grinding time of 50 s was chosen for the subsequent analysis.

A summary of the size measurement results for spray and freeze-drying powders is presented in Table 3. Spray drying

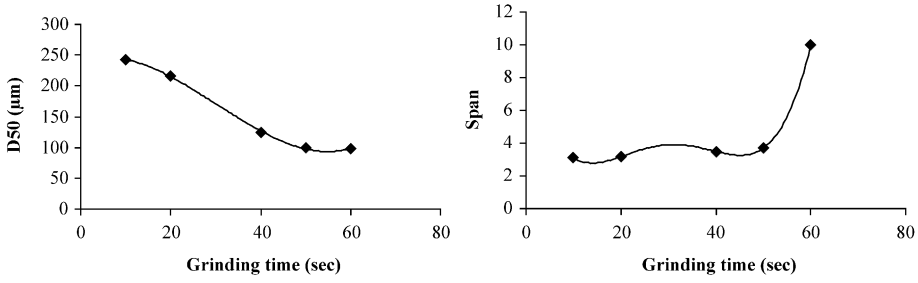

Fig. 5. Freeze-dried particles size (d_{50}) and distribution span versus grinding time.

Table 3
Size distributions of freeze-dried and spray-dried particles

	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Span
Spray drying				
Mean	14	37	84	
Standard deviation	0.51	0.80	0.94	1.87
Freeze-drying				
Mean	26	131	450	
Standard deviation	0.322	2.07	8.12	3.22

leads to small particles with an average diameter of 37 μm. The distribution span is quite large. Fine particles are present which can lead to cohesion problems. Freeze-dried particles are larger with a d_{50} equal to 131 μm. However, the size distribution is very large, which means a big size heterogeneity. Particle size is one of the most important properties for powders: those with a particle size larger than 200 μm are generally considered as free flowing. Fine powders are subject to cohesion and their flowability is more difficult [11]. Size and shape distributions affect many properties such as powder packing, fluidisation or dry mixing. Irregular particles like freeze-dried ones are more subject to frictions, which limit the motion of individual particle [12].

3.4. Residual water content

The spray-dried powder is less humid than the freeze-dried one (Fig. 6). However, the residual water content is low in both cases and acceptable for industrial application.

A low residual humidity is necessary to avoid creation of water bridges between particles and therefore agglomeration. Powder cohesiveness depends on moisture content. The less humid a powder is, the less cohesive it is and as consequence more free flowing [11].

3.5. Sorption isotherms

Thiocyanate is a very hygroscopic product. At high water activity values, the water up-take is very important.

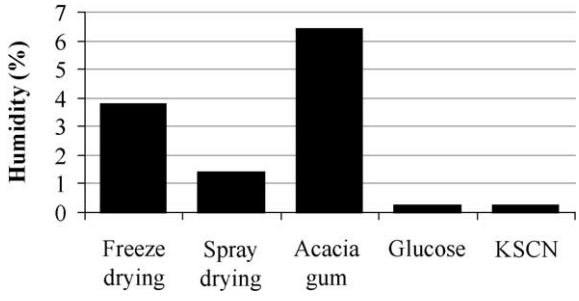

Fig. 6. Comparison of residual water content of dried powders and initial products (humidity: g of water per 100 g of solid).

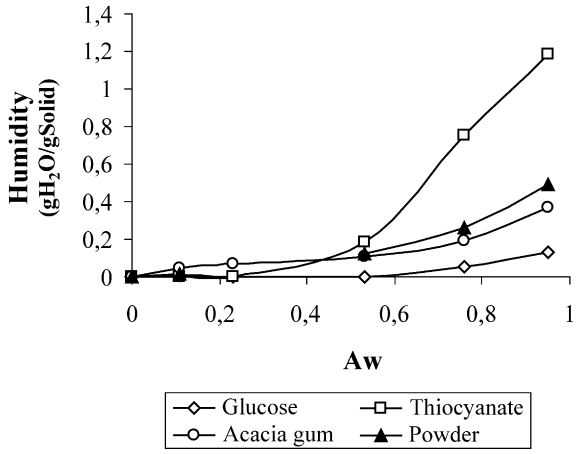

Fig. 7. Sorption isotherms of the powders and initial products in wet basis.

Glucose is the least hygroscopic of the three constituents, and acacia gum has an intermediate behaviour. Components dried mixture has the same behaviour as acacia gum alone (Fig. 7). Encapsulation of thiocyanate and glucose in a matrix of gum allows a good control of thiocyanate hygroscopicity above all at high water activity values. In those conditions, agglomeration and caking risks decrease and the powder is more stable during storage.

3.6. Surface analysis by DRIFT spectroscopy

Agglomeration and bad flowability of a powder is also due to surface particle–particle interactions. Different types of bounds can be formed between particles:

- Physicochemical forces (Van der Waals, electrostatic, hydrogen bounds)
- Solid bridges (dissolution/re-solidification).

Figs. 8–11 present, respectively, DRIFT spectra of the spray-dried and the freeze-dried powders of acacia gum and of glucose.

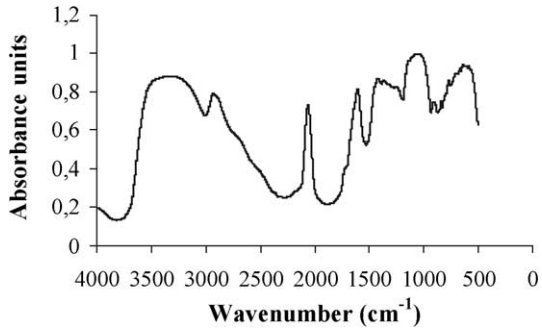

Fig. 8. DRIFT spectrum of spray-dried powder.

Table 4
IR adsorption characteristics of the main chemical functionalities (S: strong, M: medium, VS: very strong)

Functionalities		Frequency (cm^{-1})		Remarks
		Stretching	Deformation	
OH	S	3650–2500	<1680	More groups are bound with hydrogen links, more frequencies are low and bands large
NH	S	3600–2800	1680–1400	Primary amine/amide single bond, secondary amine/amide double bonds for valence modes
CH	S	2970–2845	1480–1370	Vinylic and aromatic CH groups adsorb between 3150 and 3000 cm^{-1} in the stretching mode
C═O	S	1815–1400	–	Decrease in the frequency corresponds to a loss of the double bond strength
C═C	M	1660–1620	–	In aromatic compound, frequency is located between 1650 and 1450 cm^{-1} (cycle vibration)
C–O	VS	1370–1070	–	Easy to detect. In epoxy compound, frequency can be lowered down to 950–810 and 840–750 cm^{-1}

Diffuse reflectance gives chemical information on the particle surface. To analyse the spectrum, it is necessary to take into account the absorption band position, intensity and shape. IR adsorption characteristics of the main chemical functionalities are discussed in a previous paper [13] and summarised in Table 4.

In our case, spray- (Fig. 8) and freeze-dried (Fig. 9) powders present the same spectrum than acacia gum (Fig. 10) with an additional peak at 2050 cm^{-1} corresponding to potassium thiocyanate. Those results attest of a good matrix encapsulation of glucose and thiocyanate as the gum appears on the surface of the powder. If glucose should have been on the surface, the spectrum should have been closer to the glucose one (Fig. 11), particularly in the stretching mode of CH groups between 2980 and 2845 cm^{-1}. Because of the sticky behaviour of glucose, the risk of agglomeration is then strongly decreased. DRIFT measurements allow to conclude that the two drying techniques lead to a similar encapsulation result with the same chemical surface composition.

Macroscopic observation of the freeze-dried powder allowed to think of a crystalline structure in opposition with spray-dried powder which seems to be amorphous. X-ray experiments were performed and obtained results revealed no structural difference between the two powders. Their two spectra are typical of an amorphous structure. The drying technique has no effect on the powder chemical structure organisation.

3.7. Global behaviour characterisation

In reference to Carr indices [10], the flow properties of the two powders are not good (Table 5). The floodability of the spray-dried powder is high. It is related to the stability or instability of a powder and its easiness to flow under strain. A very high floodability is characteristic of a powder which tends to flush [12]. Freeze-dried powder is less dense than spray-dried but more cohesive. Spray-dried powder is dense but above all very dispersible. For industrial application, these two powders could not be used like this.

To improve the powder flowability, it would be possible to:

- control environmental parameters such as temperature or humidity,
- adapt existing equipment which is possible for a new unit but often too expensive,
- bring energy to the system with vibrator and extractor that will increase production cost and can be difficult in a compact production chain,
- modify the powder characteristics by coating or granulation,
- use an additive to improve flow properties.

It was decided to test the two last proposals on spray-dried powder. Two additives have been used and two

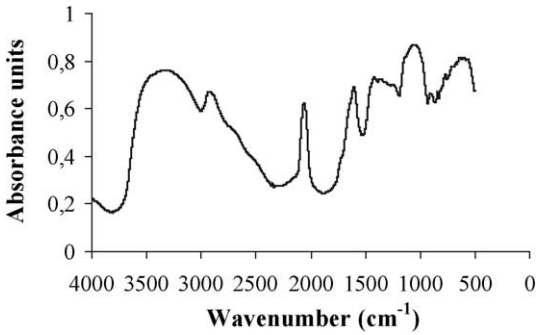

Fig. 9. DRIFT spectrum of freeze-dried powder.

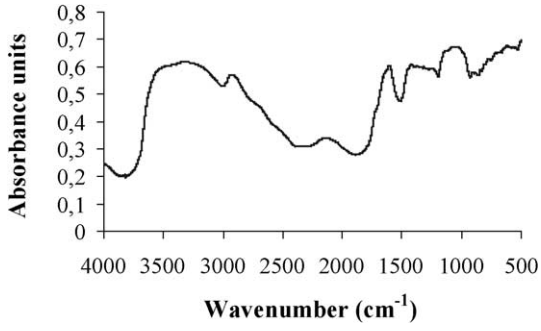

Fig. 10. DRIFT spectrum of acacia gum.

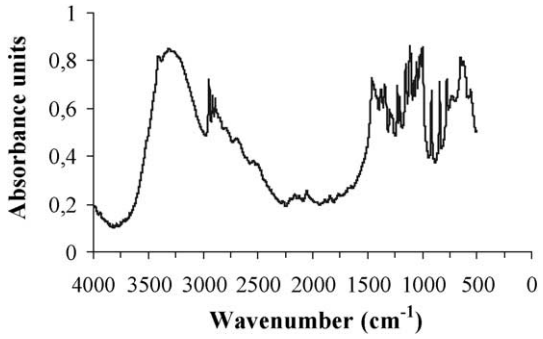

Fig. 11. DRIFT spectrum of glucose.

secondary coatings as well. The two additives are pure alpha cellulose IDA 60 often used in food industry and wheat fibre isolate ID 95 (ID FOOD, France).

The principle of action of outflow additive is to coat powder particles by adsorption of fine and fluffy particles changing cohesiveness, interaction with the support and rheological properties [14]. Four concentrations have been tested for both additives: 0.5%, 1%, 1.5% and 2% (w/w). Results are presented in Table 6.

Neither cellulose nor wheat fibre improve the flowability of the powder. This result is in line with observations made by Graindorge [14]. According to this author, there is not a universal additive, but one additive for one specific powder and in one definite condition. Therefore, the choice of an additive should be based on a complete preliminary study when different additives are tested to find conditions most appropriate to the powder and its environment.

Two types of coatings have been tested: acacia gum and carrageenan. Contrary to additives, coating reduces the number of fine particles and increases the particle size. The first acacia gum coating does not modify the other surface properties of the powder, and residual water content is similar (6.7%). The second coating with carrageenan changes size distribution and surface properties.

Table 6
Flow properties of spray-dried powder after addition of an additive, pure alpha cellulose or wheat fibre isolate at four concentrations: 0.5%, 1%, 1.5% and 2% (w/w)

	Cellulose				Wheat fibre			
	0.5%	1%	1.5%	2%	0.5%	1%	1.5%	2%
Flowability	38.5	44.5	39	40.5	44.5	42	40.5	41.5
Floodability	67	80.5	67.5	71	76	78.5	80	71.5

Secondary coating improves the flowability of spray-dried powder. After coating, its flow properties are normal (Table 7). Coating decreases angle of spatula, compressibility, angle of repose and dispersibility values and increases powder-aerated bulk density especially with carrageenan coating. Large bulk density and low compressibility are typical of more free-flowing powders. Packed bulk density and other criteria are unchanged. Coating reduces the amount of fines. Size distribution is narrower: particles with size below 10 μm disappear and the mean diameter (d_{50}) increases (results not show). As a consequence, small particles adsorption on bigger one is reduced, and particle motion and flowability improve.

In conclusion, the two powders obtained by spray and freeze-drying vary especially by the shape of the particles. Residual water content, moisturising capacity and chemical surface properties are similar. Flow properties studies show high difference between the two powders. This work confirms that the shape stays a determinant factor, which can highly modify rheological behaviour.

To choose the device, attention has to be paid on the goal of the drying and industrial considerations like cost price or number of steps. The aim of this production is to coat the two enzymes of the lactoperoxidase system (lactoperoxidase and glucose oxidase) around the dry core. According to this, it would be better to choose spray drying because it is a one-step device and the particles obtained are well rounded making coating easier. Moreover, coating will increase final size of the particles which can lead to a better outflow.

Table 5
Physical properties of the two powders in ambient conditions

	Freeze-drying	Spray drying
Angle of repose (°)	48.5	51.2
Aerated bulk density (g/cm^3)	0.273	0.478
Packed bulk density (g/cm^3)	0.432	0.814
Compressibility (%)	36.8	41.3
Angle of spatula (%)	57.4	57.2
Cohesiveness (%)	39.3	23.8
Flowability index	40	42
Angle of fall (°)	38.9	34.6
Angle of difference (°)	9.6	16.6
Dispersibility (%)	6.2	44.8
Floodability index	48	72

Table 7
Influence of acacia gum and carrageenan coatings on powder properties

	Acacia gum	Carrageenan
Angle of repose (°)	40.1	43
Aerated bulk density (g/cm^3)	0.536	0.727
Packed bulk density (g/cm^3)	0.719	0.837
Compressibility (%)	25.5	13.1
Angle of spatula (%)	44.8	55.2
Cohesiveness (%)	30.4	46.5
Flowability index	59.5	60
Angle of fall (°)	26	34.4
Angle of difference (°)	14.1	8.6
Dispersibility (%)	21.7	22
Floodability index	75	66.5

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