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Improving the dispersion kinetics of a cocoa powder by size enlargement

T.O. Vu, L. Galet*, J. Fages, D. Oulahna

Ecole des Mines d'Albi-Carmaux, Laboratoire de Génie des Procédés des Solides Divisés, UMR CNRS 2392, Campus Jarlard, F-81013 Albi, France

Abstract

The efficient dispersion of powders in liquids is required in many fields. For this reason, it is useful to understand the mechanisms of dispersion and the physical properties of powders which influence the dispersion rate. Here, we have chosen to work with a low fat cocoa powder commonly used in the food industry. Firstly, we have determined the physical properties of the powder (densities, cohesion, flowability, size and surface energy) and then measured the dispersion times of cocoa in water using a novel optical method. Further experiments, using the same technique, are performed using larger grains obtained by granulating cocoa powder. It is found that the dispersion times are shorter for the granules and much shorter than the dispersion time for ungranulated powder. The dispersion times for granules increase with the size of granules

1. Introduction

Powders are often used in industry in the form of dispersion in a liquid. This is the case for cements, paints, pharmaceuticals and food powders. The different steps in powder dispersion are wetting, immersion, sedimentation and disintegration. These different processes are affected by the way the operation is carried out: how the powder is poured into the liquid, how mechanical energy is used to stir the liquid, and also by the physical and chemical properties of the dispersing liquid (surface tension, density and viscosity) and by the physical and chemical properties of the powder itself (particle size, density and surface properties). The latter can be modified by granulation and have a large effect on the dispersion kinetics.

Few studies have dealt with the physicochemical parameters involved in the dispersion of a powder in a liquid. In the food industry, different authors have begun to study the use of granulation to obtain instant powders [1–5], but these studies often lack generality and do not deal with the importance of each parameter separately and how they interact together to control the dispersion kinetics. The study reported here is concerned with these factors.

The system chosen for study is cocoa powder in milk or water. This is an often encountered case of an insoluble,

hydrophobic, but easy to formulate powder, which is hard to disperse in milk or in water. We first present some physical characteristics of the cocoa powder, the experimental conditions used to granulate it and the novel method used to follow the dispersion of cocoa particles in water. Finally, we show the size influence of the dispersion of cocoa granules in water.

2. Materials and methods

2.1. The cocoa powder

2.1.1. Physical properties

The cocoa powder used in this study has been characterised in terms of particle size, flowability, surface free energy and various density measurements (true, aerated and packed density). The size distribution was measured with a Malvern 2000 laser diffraction instrument as a suspension in water. The true solid density was measured by means of a Micromeritics Accupyc helium pycnometer. Aerated and packed densities were measured using a Hosokawa PTN, a powder tester. The porosity was measured with a Micromeritics mercury porosimeter.

2.1.2. Surface free energy

Stevens' method [6,7] was used to determine the surface energy of cocoa powder. The method consists in sprinkling the powder on the surface of solutions of known surface

* Corresponding author. Tel.: +33-5-63-49-32-35; fax: +33-5-63-49-30-25.

E-mail address: laurence.galet@enstimac.fr (L. Galet).

Table 1
Physical properties of cocoa powder

Mean particle size (μm)	d_{50} 16
Span : $(d_{90} - d_{10})/d_{50}$	2.2
True density (g cm^{-3})	1.44 ± 0.01
Aerated density [D_{aerated}] (g cm^{-3})	0.34 ± 0.01
Aacked density [D_{packed}] (g cm^{-3})	0.67 ± 0.01
Porosity (by mercury) (%)	20 ± 2
$I_{\text{Carr}} = (D_{\text{packed}} - D_{\text{aerated}})/D_{\text{packed}}$	49% very bad flowability
$I_{\text{Hausner}} = D_{\text{packed}}/D_{\text{aerated}}$	1.96 very cohesive
Surface free energy (mN m^{-1})	$40 \leq \sigma \leq 50$

tension. These solutions are composed of mixtures water and isopropanol in different ratios. The value of the powder surface energy is taken to be that of the surface tension of the mixture for which the sprinkled powder is wetted in less than 1 min.

2.1.3. Results

The main characteristics are summarised in Table 1. The aerated and packed densities (D_{aerated} and D_{packed}) are used to calculate the Carr and Hausner indexes (I_{Carr} and I_{Hausner}) [8], which characterise, respectively, the flowability and the cohesive forces of a powder.

$$I_{\text{Carr}} = \frac{D_{\text{packed}} - D_{\text{aerated}}}{D_{\text{packed}}} \quad (1)$$

$$I_{\text{Hausner}} = \frac{D_{\text{packed}}}{D_{\text{aerated}}} \quad (2)$$

The intraparticle porosity of cocoa powder is about 20% with a pore size range from 1 to 5 μm . The median particle size is quite low (16 μm), but the size distribution is wide (span=2.2). The powder is very cohesive and the flowability is bad. The surface energy is less than surface tension of water (72 mN m^{-1}) meaning that the cocoa powder is not wetted by water.

2.2. Formulation

2.2.1. Wet granulation

The cocoa powder was agglomerated by wet granulation in a Diosna high shear mixer granulator using the experimental conditions given in Table 2. The binder water was added in drips, and the granules were dried in an oven at 45 $^{\circ}\text{C}$ for 5 h then separated in five size classes by sieving.

Table 2
Wet granulation conditions

Mass of cocoa powder (g)	200
Water ratio: (mass water/mass powder) (%)	65
Water flow (g s^{-1})	0.62
Speed rotation (rpm)	300
Water addition time (s)	210
Granulation temperature ($^{\circ}\text{C}$)	25

Table 3
Size, mass fraction and granule porosity

Class	Size (μm)	Mass fraction (% \pm 0.1%)	Mercury porosity (% \pm 2%)	Flowability	Cohesion
1	$d < 200$	30.0	21	good	low
2	$200 < d < 630$	22.1	17	good	low
3	$630 < d < 1000$	13.3	20	good	low
4	$1000 < d < 2000$	24.6	20	good	low
5	$2000 < d$	9.9	21	good	low

2.2.2. Characteristics of the granules

The characteristics of each granule size class are given in Table 3: mass fraction, intragranular porosity and flowability properties. We can observe that the intraparticle porosity seems to be constant for all the granule size classes. The cohesion is low, and the flowability of each class is good.

3. Dispersion time measurement

Several different methods are currently used to measure dispersion times [1]. In particular, Crawley et al. [9] used a turbidimetric measurement, which has many advantages, e.g. simplicity, continuous on line measurements and easy calibration. However, in the case treated here, cocoa particles are absorbent and give opaque suspensions, thus making it difficult to observe the different phenomena involved in the dispersion and rendering conventional turbidimetry impossible. For this reason, a novel optical method based on an optical fibre bundle sensor has been used. This allows the determination of the fluctuations of volume concentrations and size in a suspension, which can be interpreted in terms of the quality of dispersion.

3.1. Description of the optical technique used

The technique used [10] is based on a bundle of optical fibres of which a central optical fibre emits light (Fig. 1) and the light back scattered by the particles in the suspension is collected by a six fibre crown around the central fibre. An electronic system converts the back scattered light intensity into a voltage, and a data acquisition system stores the voltage as a function of time.

This optical fibre sensor can be calibrated against solids volume fraction for quasi spherical particles. In this case, if

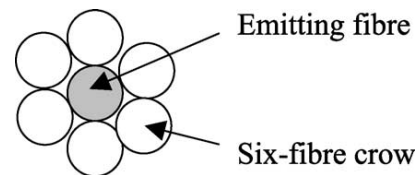


Fig. 1. Optical fibre bundle sensor.

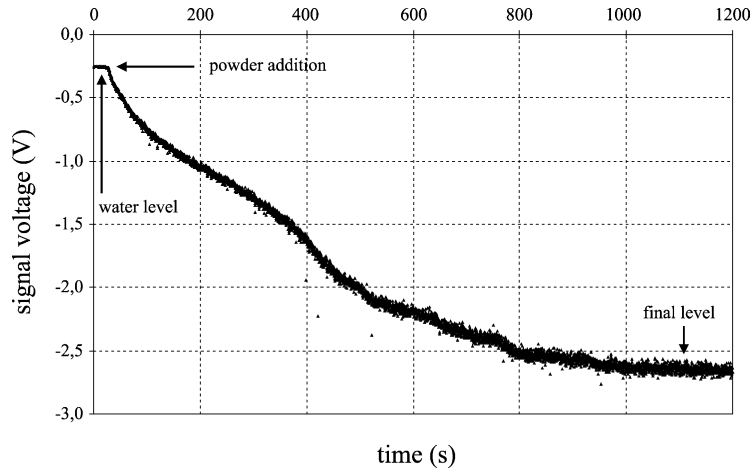


Fig. 2. Data acquisition curve for $C_v = 1.03\%_v$ at 470 rpm.

the volume fraction of particles is known, it is possible to obtain the mean diameter of the dispersed particles [10]. In the case here, we determine the time to obtain the final voltage for dispersed particles in water suspension.

3.2. Measurement conditions

The apparatus must be calibrated with different volume ratios of cocoa. This is done by introducing a known amount of cocoa into 2 l of water and thoroughly mixing by mechanical agitation until complete dispersion is obtained. The corresponding voltage is then measured. Preliminary experiments show no effect of the location of the optical fibre bundle in the reservoir on the dispersion kinetics.

The second step is the measurement of the dispersion time of unprocessed cocoa powder. The whole mass of cocoa is poured in one movement onto the water surface without it being aerated by sieving. This measurement is performed at room temperature (22 ± 1 °C) for different cocoa to water

ratios. The instrument signal is observed to decrease as the powder becomes dispersed, and we stop the acquisition when a steady level is attained. Stirring is by a turbine agitator giving a mechanical energy per volume of about 90 and 870 W/m^3 at 470 and 1000 rpm, respectively.

An example of a signal against time curve is given in Fig. 2 corresponding to an experiment where 30 g of cocoa were dispersed in 2 l of water ($1.03\%_v$) at 470 rpm agitation. The initial level corresponds to the water signal, and the signal decreases during dispersion to the final level, which corresponds to the maximum dispersion attainable under the experimental conditions. V_{X° is calculated as:

$$V_{X^\circ} = \frac{V_X - \bar{V}_{\text{water}}}{\bar{V}_{\text{final}} - \bar{V}_{\text{water}}} \quad (3)$$

Fig. 3 shows V_{X° versus time. A difference $\bar{V}_{\text{final}} - \bar{V}_{\text{water}}$ of 100% corresponds to total dispersion. The dispersion time is taken as the time elapsed between 90% and 10% of $\bar{V}_{\text{final}} - \bar{V}_{\text{water}}$. This method of treating the signal gives a

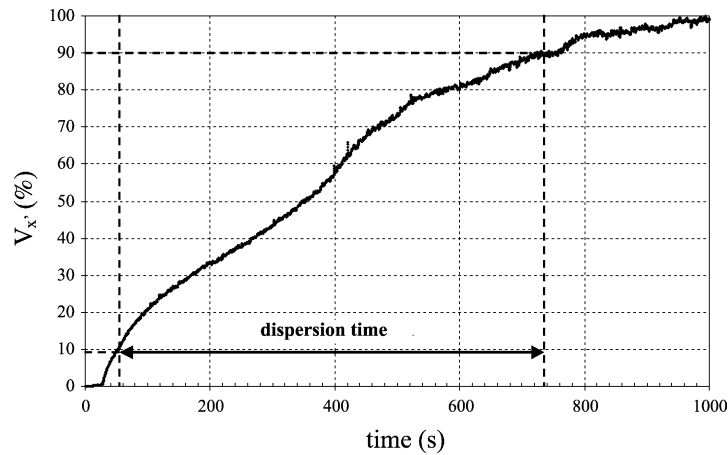


Fig. 3. Experimental dispersion curve for $C_v = 1.03\%_v$ at 470 rpm.

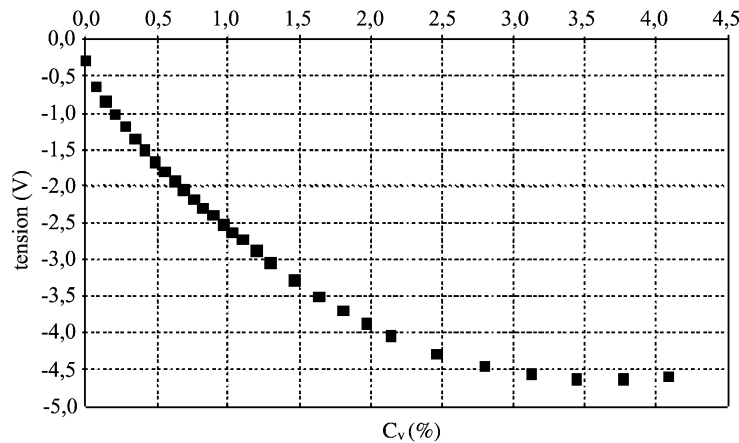


Fig. 4. Calibration curve for cocoa powder in 2 l of water at 630 rpm.

precision on the determination of the dispersion time of about 5%.

4. Results and discussion

4.1. Calibration curve

The calibration curve of voltage (V) versus cocoa concentration (%) obtained by successive additions of cocoa is given in Fig. 4. It can be seen that, as light is back scattered by the cocoa particles, the signal decreases as the cocoa/water ratio increases. After a critical amount of powder has been added, the signal is saturated and the voltage no longer changes with the amount of cocoa. For the rest of this study, a concentration less than 3%, is used.

4.2. Unprocessed powder

The dispersion time and the rate of dispersion have been measured for different concentrations of cocoa (C_v from 0.35% to 2.08%) and for two stirrer speeds. The first stirring rate is called medium (470 rpm) and the second is called a

high (1000 rpm). The time of dispersion (s) and the dispersion rate (g s^{-1}) are given in Table 4, and the curves of dispersion versus cocoa concentrations (%) are shown in Figs. 5 and 6. The mean dispersion rate (in g s^{-1}) is calculated with Eq. (4). For all experiments, the reproducibility on the dispersion time is about 5%.

$$r = \frac{m_{\text{cocoa}}}{t_{\text{dispersion}}} \quad (4)$$

At the medium stirring rate (470 rpm), the dispersion times are long. Several minutes are required to disperse only 10 g of cocoa (0.35%). From 0.35% to 1.35%, the dispersion rates are very low, less than $5.3 \times 10^{-2} \text{ g s}^{-1}$. We observe that the dispersion rate is small and increases slightly with the cocoa concentration. For the two higher concentrations, the powder was not at all wetted by water and some powder remained on the surface for a long time (more than 30 min). A steady level is not attained, dispersion is not complete and no dispersion time can be attributed.

With high speed stirring (1000 rpm), the dispersion times are much lower and a dispersion time can be attributed for all

Table 4
Dispersion time and dispersion rate as function of concentration (470 and 1000 rpm, 2 l of water)

Cocoa powder		Dispersion time (s)		Mean dispersion rate (10^{-2} g s^{-1})	
Mass (g)	C_v (%)	470 rpm	1000 rpm	470 rpm	1000 rpm
10	0.35	378	48	2.6	20.8
20	0.69	616	62	3.2	2.3
30	1.03	671	80	4.5	37.5
40	1.36	760	154	5.3	26.0
50	1.70	α	16	$\rightarrow 0$	312.5
60	2.08	α	12	$\rightarrow 0$	500.0

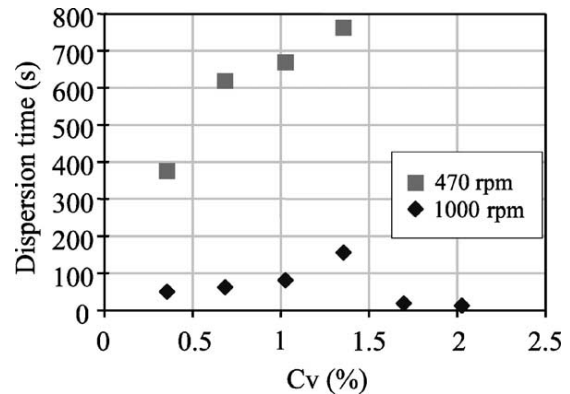


Fig. 5. Dispersion time versus concentration for 470 and 1000 rpm.

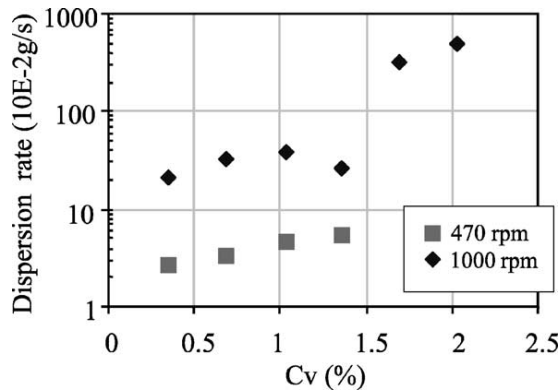


Fig. 6. Dispersion rate versus concentration for 470 and 1000 rpm.

concentrations. In this case, the dispersion time increases with all concentrations as observed at 470 rpm, except for the results at 1.7%_v and above. High concentrations of cocoa powder give a very short dispersion time as the whole quantity of cocoa powder penetrates directly into the water without staying on the surface. From 0.35%_v to 1.03%_v, the dispersion rate increases with increase in concentration from 20.9×10^{-2} to $37.5 \times 10^{-2} \text{ g s}^{-1}$. At higher concentrations, the dispersion rate increases rapidly with concentration.

4.2.1. Medium agitation speed (470 rpm)

Fig. 5 shows that the dispersion times are very long for free cocoa powder (more than 6 min for 0.35% and more than 12 min for 1.35%). In the experiment at 1.70%, the dispersion time cannot be measured. In fact, mechanical stirring of 470 rpm is insufficient to disperse cocoa powder. A bed of powder remains on the surface of water, with a viscous layer stopping capillary flow in the intergranular porosity, and the agitation is not sufficient to make the cocoa layer penetrate into the bulk liquid. This bad dispersion behaviour is caused by a number of phenomena. One is the hydrophobic nature of cocoa, the fat content being 10–12% in cocoa powder, so that the surface energy of the powder is lower than the surface tension of water. Capillary rise experiments confirm the very low wettability of the cocoa powder. In this technique, a bed of cocoa powder 1 cm height (0.5 g of cocoa powder into a glass column of 1 cm diameter supported by a thin sintered glass disk) is placed just touching a water surface, and the mass of water taken up

Table 5
Dispersion of cocoa granules $C_v = 1.03\%$, 470 rpm

Class	Size (μm)	Dispersion time (s)	Dispersion rate (10^{-2} g s^{-1})
1	$d < 200$	88	33.8
2	$200 < d < 630$	299	10.1
3	$630 < d < 1000$	266	11.3
4	$1000 < d < 2000$	464	6.5
5	$2000 < d$	861	3.5

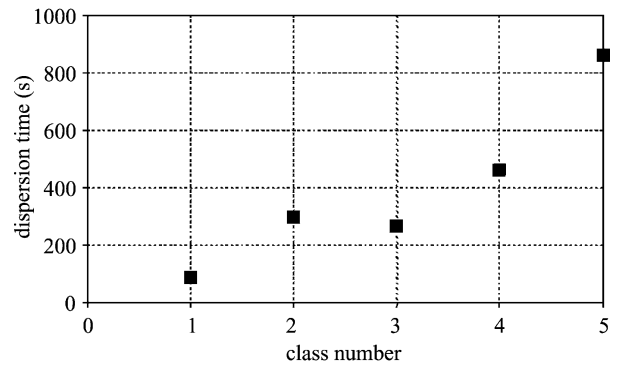


Fig. 7. Dispersion time of cocoa granules, $C_v = 1.03\%$, 470 rpm.

by capillary in the cocoa powder is measured as a function of time. We observe that after 30 min, only a small part of the cocoa powder bed is wetted by the water (less than 0.4 g of water in 30 min).

Another factor which has an influence on the quality of dispersion is the size of the grains [3]. The smaller the grains, the more difficult is the dispersion. No penetration occurs even though the solid density is greater than the density of the water because the significant factor is the aerated and packed densities (0.34 and 0.67 g cm^{-3}) of the powder bed which are lower than that of water. The powder bed does not naturally penetrate the water surface, and the system requires mechanical energy.

Another reason for the bad dispersion is the bad flow ability and the cohesive forces of powder (I_{Carr} and I_{Hausner}). It seems that this cohesion causes the formation in the powder of solid agglomerates, and the shear forces are not sufficient to break the cohesive forces between grains.

4.2.2. High agitation speed (1000 rpm)

It can be seen in Fig. 5 that at 1000 rpm, the dispersion times for all amounts of cocoa are very low and less than for 470 rpm. There is no longer a cocoa bed on the surface whatever the concentration is, and the dispersion time increases with concentration for 470 rpm. The dispersion rate increases (Fig. 6) with concentration as the mechanical

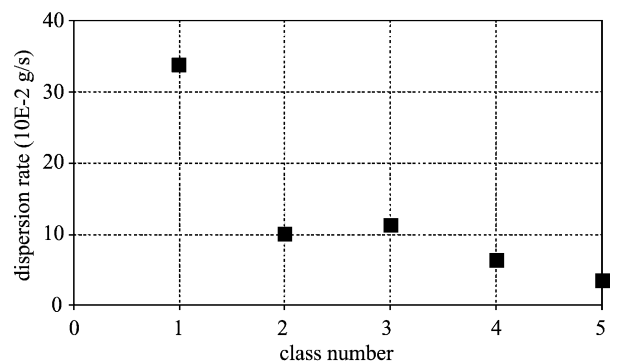


Fig. 8. Dispersion rate of cocoa granules, $C_v = 1.03\%$, 470 rpm.

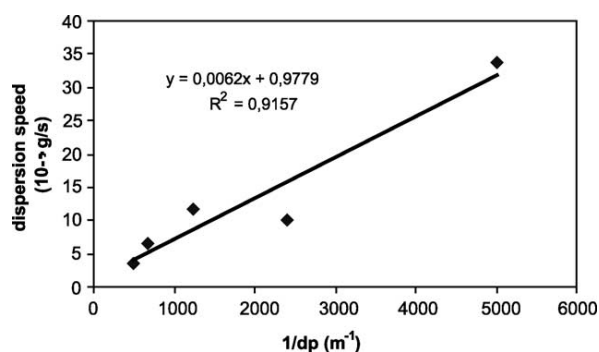


Fig. 9. Dispersion rate of cocoa granules in function of $1/d_p$, C_v 1.03%, 470 rpm.

energy is sufficient to break the cohesive interaction between the cocoa particles. The behaviour for concentrations greater than 36% does not follow this reasoning and for the moment remains without explanation.

4.3. Granulated cocoa powder

Experiments have been performed with cocoa granules (see I.2.) dispersed in water at 1.03%_v (30 g in 2 l). The dispersion time and the dispersion rate were measured for each granule size class and are given in Table 5. It should be noted that all the granules have the same intragranular porosity.

The dispersion times determined for the five granule size classes are shown in Fig. 7. It can be seen that the dispersion times increase with granule size. Dispersion time is very short for small granules (about 90 s are required to disperse 30 g of granules less than 200 μm) and quite long for big granules (about 860 s are required to disperse 30 g of granules of size greater than 2000 μm). However, there is an improvement with respect to the unprocessed powder for all classes except class 5 ($d > 2000 \mu\text{m}$). It should be noted that no undispersed granules remain in the suspension at the end of the experiment. Fig. 8 shows the corresponding change in dispersion rate with concentration.

In comparison to the unprocessed cocoa powder, the dispersion time is improved for all the granules less than 2000 μm . For granules of this size, the dispersion time is higher than that of the unprocessed powder at 861 and 671 s, respectively.

In contrast to the unprocessed powder, the granules penetrate instantly into the liquid where they are broken by the mechanical agitation. The dispersion time is improved because one step is eliminated in the dispersion process. The granulated cocoa powder has a good flowability and the granules are not cohesive. Therefore, the cohesive forces between granules are low and shear forces at the suspension surface are sufficient to separate the granules without requiring a high mechanical energy.

For the largest particle size class, the same phenomena occur but the breakage of these large agglomerates is more

difficult and takes longer. Water penetrates into the intra-particulate pores to the heart of the granule, but as the granule radius is greater, this step takes longer and is harder to do. Capillary flow into the granules is slow and breakage is not complete. This hypothesis is confirmed by the final voltage level, which is higher than the expected value, indicating that dispersion is not complete and the particle size of the dispersion is higher than the unprocessed grain size. The dispersion time is no longer improved by an increase in granule size. It seems that dispersion depends on the external surface of the granules. Fig. 9 shows a linear evolution of the dispersion rate as a function of $1/d_p$ (d_p is the granule diameter), which is proportional to the specific surface of the granules. Before drawing a final conclusion about this relation, it is necessary to perform further experiments with narrower size classes.

5. Conclusion

A novel optical method has been used to measure dispersion times and is shown to give interpretable results for a cocoa powder/water system. The method is reliable for these opaque suspensions and the measurements are accurate.

It is found that it is hard to disperse cocoa powder, but things can be improved by a greater stirrer. Dispersion rates of cocoa can be improved by using wet granulation to increase the size of particles. Further work is in progress to measure the effects of granule porosity and pore size on dispersion kinetics and on the dispersion rates for cocoa sugar mixtures.

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