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IMPACT STRENGTH DISTRIBUTION OF PLACEBO ENZYME GRANULES

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ABSTRACT

Enzyme granules are used in laundry detergent formulations to improve washing quality at lower temperatures than commonly used with traditional formulations. However, any dust generated from their handling in manufacturing plants poses a health risk to operators. Therefore, current enzyme granule manufacturing produces strong granules that resist plant stresses and hence do not easily break. There are however indications that a very small number of granules are substantially weaker than the rest. This would have implications on the Coefficient of Variations (CV) of enzyme dust analysis. It is highly desirable to have a low value of Coefficient of Variation (CV) of enzyme dust to ensure confidence in the test results. The CV is largely influenced by the testing rig performance, but its minimum value is limited by the material characteristics. This work sets out to evaluate the minimum CV that is possible to get for the sample mass tested, by quantifying the number of outliers by impact testing using placebo granules. The outcome is a methodology for specifying the minimum possible CV that can be obtained from a given test material.

KEYWORDS: Coefficient of Variation; Outliers; Enzyme granules

1. INTRODUCTION

Enzyme granules are protein-based materials, which are used to speed up the chemical reactions. They are widely used in detergent powders to wash away the stains, fat, tough starch and soils that are not readily removed by surfactants alone [1]. The current enzyme granule manufacturing produces strong granules; however, a very small number of them are weak, and prone to breakage. The protein dust (particles smaller than 100 μm) can potentially cause respiratory allergy and asthma, as investigated in the late 1960’s by Pepys et al. [2] and Flindt [3], and the effects of the enzyme dust on the workers in a detergent manufacturing plant have been reported by Sarlo et al. [4] and Vanhanen et al. [5]. Hence, it is very important for manufacturing to examine the dustiness and strength of the enzyme granules. Currently there are number of methods and devices used to evaluate the strength and dustiness of the enzyme granules, such as the Heubach [6] and Elutriation test devices [7].

The Heubach test device is commonly used to evaluate the strength of the enzyme granules. It consists of four steel balls which are driven over a bed of granules. The balls apply force onto the granules, and have a milling effect. Dust and debris are generated as a result of the granule-granule and granule-wall contacts. The dust is collected on a filter, and is analysed for protein content by protein active assay or enzyme-linked immunosorbent assay (ELISA) [8], and is usually reported per unit mass of total dust or volume of air sampled [9]. The mass of granules used in the device is around 20 g [6, 10]. The main disadvantage of this method is that the stresses in this method might not be representative of the actual plant stresses, and also the type and level of the stresses cannot be changed [9].

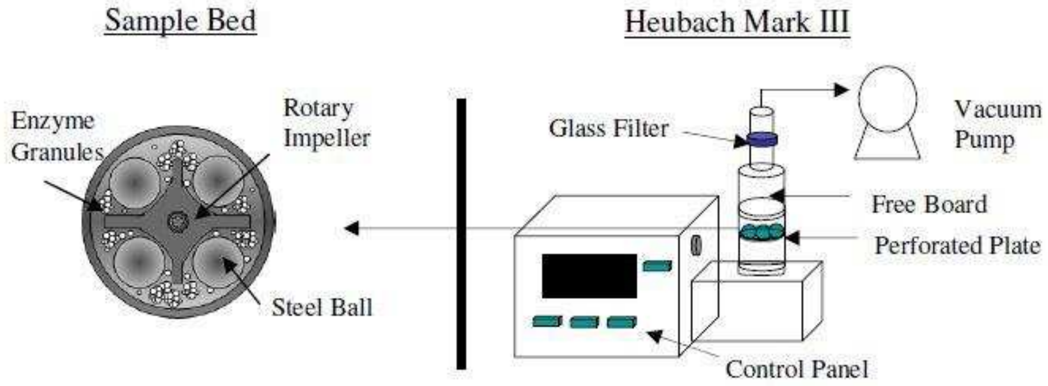


Figure 1. Heubach test device with steel balls and impeller [7]

The Elutriation test device is used in detergent industries in order to examine the dustiness of enzyme granules [7]. 60 g of granules are used in a fluidised bed (air velocity between 0.3-0.8 m/s) in a glass tube with a 1.8 m length for 30 to 40 minutes [10]. The air is passed by a bed of silica gel to adsorb the moisture, and it is then used to make the granules fluidised. Boerefijn et al. [11] and Bentham et al. [12] have studied the dynamics of the jetting region and particle attrition therein; however, estimating the contact forces is not easy, and needs modelling of interparticle collisions. The particles in the Elutriation device collide with each other. Dust is released from their surfaces and is collected from the air stream on a glass fibre filter, and is used for enzyme assay. The device is shown in Figure 2.

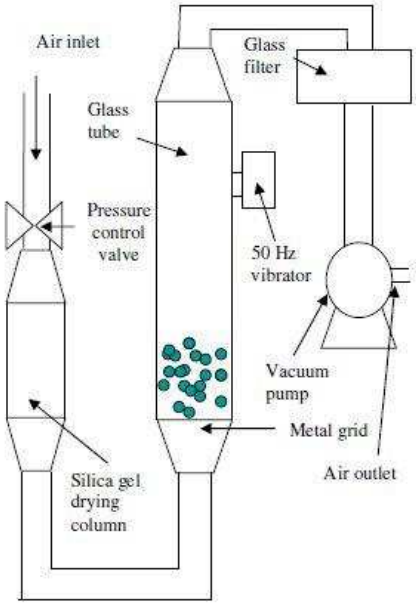


Figure 2. Schematic diagram of Elutriation test device [7]

The disadvantage of Elutriation test device is that the level and type of the stresses in the device might not be representative of the actual plant stresses [9] as of Heubach. Therefore a new device, Particle Shear and Impact (PSI) has been designed at the University of Leeds, and developed in a collaborative project between the University of Leeds, Hosokawa Micron Ltd, Runcorn (UK), and the Enzyme Dust Consortium, comprising Du Pont (USA), Henkel (Germany), Novozymes A/S (Denmark), Procter and Gamble (UK) and Unilever (UK). The device and its schematic diagram are shown in Figure 3.

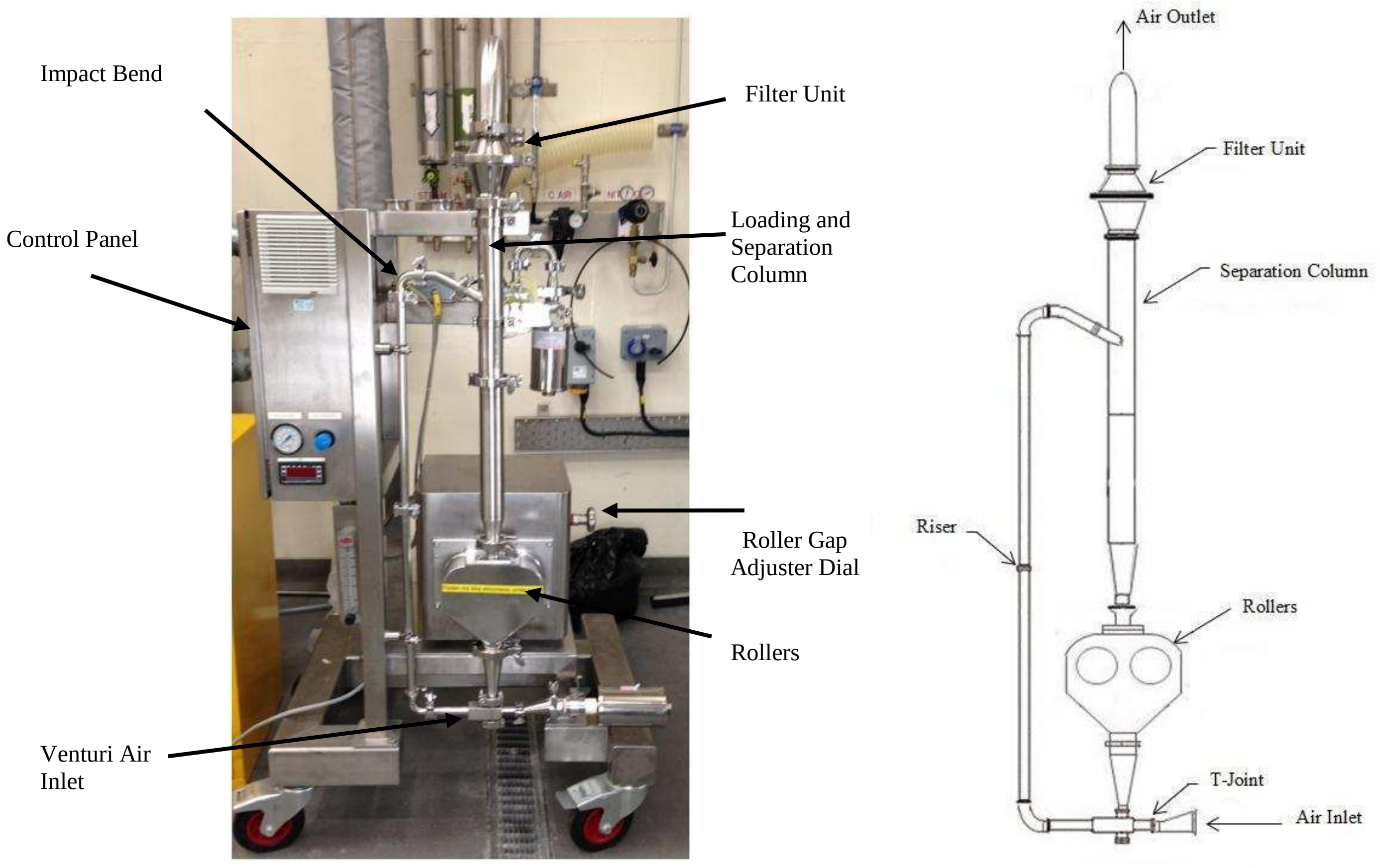


Figure 3. left) PSI tester; right) schematic diagram of PSI tester

PSI tester evaluates the strength of the enzyme granules under coupled impact and shear stresses. The granules are fed into the device and are recirculated by an air flow, and impacted onto two L-bends in the device. They then enter the separation column tangentially and are separated from the air stream. The granules fall onto a moving bed of granules on top of two counter-rotating rollers moving at different speeds behind the front panel. The angular velocity of the rollers can be adjusted independently to set a specified shear rate. As the particles pass by rollers, they experience shear deformation and may break if their strength is smaller than the contact force. The latter is controlled by the gap width between the rollers, and is adjusted to represent contact force levels prevailing in a typical plant operation. Ahmadian [9] evaluated the types and levels of stresses in a generic plant, and the PSI tester was designed to simulate such range of stresses and impact velocities. The dust and debris are collected on the filter, and are used for enzyme analysis. Both effects of impact and shear are considered in this device as shown in Figure 4, and the level of the stresses can be changed by changing the impact velocity as well as the roller gap width.

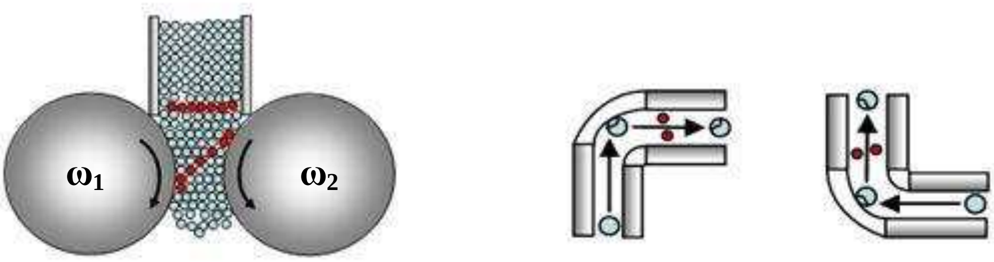


Figure 4. Particle shear and impact tester. left; a bed of granules undergoing shear by the rollers, right; impact onto L-bends

However in all these devices the variation of released enzyme dust is very wide, although its exact source is difficult to identify. Adhesion of enzyme dust to surfaces, handling losses during enzyme analysis and variation of enzyme release from damaged/ fragmented granules are most likely contributory factors. Furthermore, the enzyme granules themselves have a distribution of strength, arising from the manufacturing process itself. The variation is expressed in terms of the Coefficient of Variation (CV), which is the ratio of the standard deviation to the mean, i.e a measure of the variability of a series of measurements [13]. The CV of mass fraction of debris/dust and that of the enzyme content are obviously influenced by the testing rig operation as well as material characteristics, but its minimum value is limited by the latter. Enzyme granules are manufactured to be strong and attrition resistant with their outer layers free from enzyme content, so that the debris released from their surfaces is inert. However, there are indications that a very small number of granules are substantially weaker than the rest, and hence the fragmentation of one or two single granules could release a large quantity of enzyme. Therefore if in repeated test runs to establish the mean and standard deviation, only a small number of granules break, a large CV is recorded, making the data statistically unreliable. A question which naturally arises is the minimum granule mass requirement for getting statistically reliable enzyme dust data. Unfortunately this is inevitably fixed by the standard operating procedure for each test device. So the question can be reformulated in another form: for a given enzyme granule type/ source and mass, what is the expected CV based on material characteristics alone, i.e. independent of the test device? Therefore this work sets out to evaluate the minimum CV by quantifying the number of broken granules by impact testing using placebo granules.

Impact testing is preferred in comparison with the quasi-static side crushing test for two reasons: (i) the granule strength has such a narrow distribution that a very large number of granules has to be tested to identify the number of outliers, for which impact testing is much faster; (ii) for materials failing in the semi-brittle failure mode, impact strength is lower than quasi-static crushing strength, thus making it easier to identify the outliers. The CV obtained in this way is representative of the CV of the test material, whilst the CV obtained by the current test devices is influenced by both device operation and material characteristics. Therefore the outcome of this evaluation provides a methodology for specifying an acceptable CV to bench mark the performance of the two established methods, i.e. Heubach and Elutriation devices as well as the newly developed PSI tester.

2. METHODOLOGY AND MATERIAL

Placebo enzyme granules have been used as a test material in this work. The granules have been classified into different sieve size cuts by mechanical sieving. To evaluate the impact breakage of the granules the single particle impact test rig at University of Leeds has been used. The impact tester is a modified design of the single particle impact apparatus developed by Yüregir et al. [14]. A schematic diagram of the impact tester is shown in Figure 5.

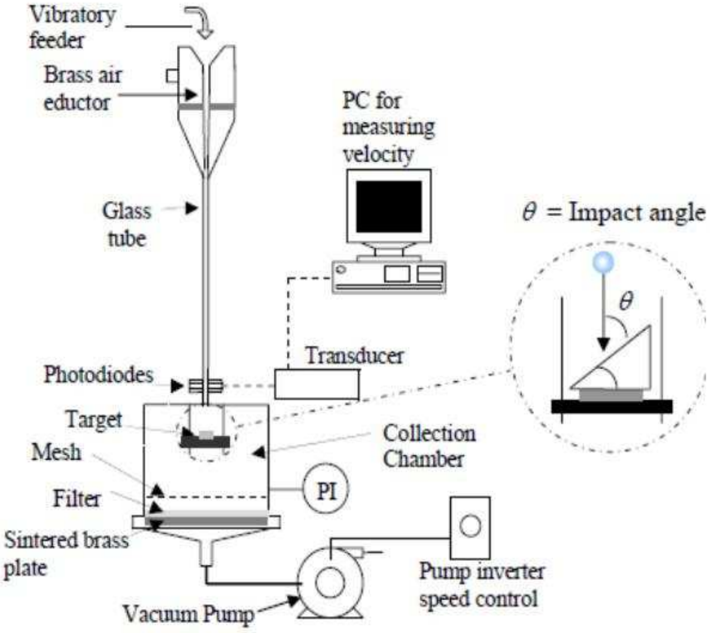


Figure 5. Single particle impact rig [15]

Impact testing has been widely used to investigate the breakage behaviour of different materials such as polymethylmethacrylate [16, 17], lactose [18], glass [19], sand [20], concrete balls [21, 22], aluminium oxide particles [23], agglomerates of glass beads [24], detergents [25] and enzyme granules [26].

For impact testing of the granules in this work, 45 g of granules are fed into the device by using a vibratory feeder. However this is done by first classifying the whole granule size distribution into nine separate sieve cuts from 250 µm to 1180 µm and testing each sieve cut separately. In this way the impact velocity for each sieve size cut is better controlled and the fragments and debris for each sieve size cut can be quantified. The particle size distribution of the placebo enzyme granules is shown in Figure 6, based on sieving and gravimetric analysis. The particles impact onto a target at 90° (the angle of impact can be changed by using different targets). The vacuum line is used to apply different impact velocities. The impact velocity has been set to 10 m/s, as it is within the range of impact velocities prevailing in a typical plant [10], which is between 5 m/s to 20 m/s.

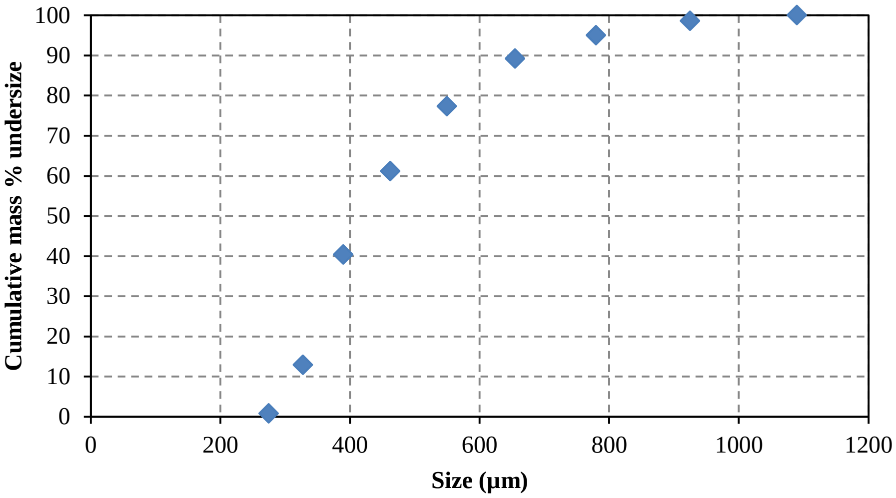


Figure 6. The cumulative mass percentage undersize of placebo enzyme granules based on sieving and gravimetric analysis

After impact testing the material is collected, and the fragments and debris are separated from the mother particles, and analysed according to the following procedures. Two different methods of separation and determination of the broken number of granules were explored. In the first method all the fragments were manually separated from the unbroken mother particles for further analysis as described below. In the second method the fragments and debris were separated by sieving, using two sieve sizes below the feed lower sieve size, and their mass was used to calculate the number of broken granules.

The first method is based on the actual observation of the broken granules, and is hence called the 'observed number of broken granules'. In this method the number of broken granules is obtained by virtually reconstituting a broken particle through observation by eye. There are different possibilities to match the fragments in order to make one single granule: two equal-size fragments, three or four small fragments, or one large fragment together with one or two small ones. Two fragments reconstituting a single granule are shown in Figure 7. As there are a large number of fragments, separated from the mother particles, the fragments reconstituting a broken one cannot obviously be related to the same original mother granule. Nevertheless in terms of determining the total broken number, matching fragments based on size and shape to form a granule by visual inspection provides a reliable method, short of impacting and recovering around 0.5 million granules individually. In this analysis method the surface damage is not considered. The enzyme granules are structured with no enzyme content in the outer layers, so the resulting debris is enzyme free, and its exclusion is not only detrimental to the analysis, but actually desirable.

Figure 7. Fragments of one single granule

The second method is based on an estimation using the mass of debris and fragments, which is called the ‘calculated number of broken granules’. The method uses the mass of the broken granules for each sieve cut, the arithmetic mean of the sieve cut, representing the average particle size, and particle density, assuming a spherical shape. The number of broken granules is then calculated by using Eq. (1).

$$Number\ of\ broken\ particles = \frac{Mass\ of\ broken\ partricles}{Particle\ density\ \times Average\ volume\ of\ one\ particle}$$

Eq. (1)

In order to assess the reproducibility of the broken number of granules for the quantity of granules tested, it is important to explore the probability of having the same number of broken granules when the test is repeated. The Poisson distribution gives the probability of a specified event occurring in a fixed interval of time or space. It is applicable to cases in which a large number of factors influence the outcome. In its early applications, Bortkiewicz [27] investigated the number of soldiers in the Prussian army killed accidently by horse kicks. In our case here, we use it to describe the failure of a very small number of enzyme granules from a very large population, as influenced by the manufacturing process. The enzyme granules are inherently very strong and only a few break out of many thousand granules, so for the mass used in the test (45 g) it is desirable to establish the CV of the number of broken granules. This is done using the Poisson distribution (Eq. (2)), for which the coefficient of variation of the number of broken granules is given by Eq. (3).

$$P(x,\lambda)=\frac{e^{-\lambda}\lambda^{x}}{x!} \qquad \text{Eq. (2)}$$

$$CV={}^{1}/_{\lambda^{0.5}} \qquad \text{Eq. (3)}$$

where λ, x and CV are the mean of the distribution, number of occurrence and coefficient of variation, respectively. In this work, λ is the number of broken granules.

3. RESULTS AND DISCUSSION

As stated previously, the granules are impacted at 10 m/s using 45 g of sample but in narrow size cuts obtained by sieving. Choosing adequate sample mass is very critical, as it needs to be representative of the whole sample in order to get ~~a~~ reliable results as well as an acceptable standard error [28]. This is obviously unknown a priori, as the spread of the impact strength distribution is not known before testing. The above mass used in the tests corresponds roughly to about 0.5 million of granules. The ensuing analysis based on the Poisson distribution will quantify the CV associated with the mass used here.

A comparison of the results for the number of broken granules obtained by the two methods is shown in Figure 8. The number of broken granules obtained by the calculation method is larger than that obtained by observation. In the ‘calculated’ number of broken granules, the mass of dust and debris is attributed to the broken granules, and this should give rise to a larger number of broken granules. The ‘observed’ number of broken granules is based on visual observation, and is considered to be more representative, as it excludes the dust and debris from surface chipping. Surface damage is not considered to affect the integrity of the enzyme granules and it does not contribute to enzyme assay [10]. Furthermore there are shortcomings in the calculation of the volume of particles for the sieve size in the ‘calculated’ method. So the results based on the calculated number of broken granules should not be taken as representing the actual breakage, and therefore this analysis method is not pursued further.

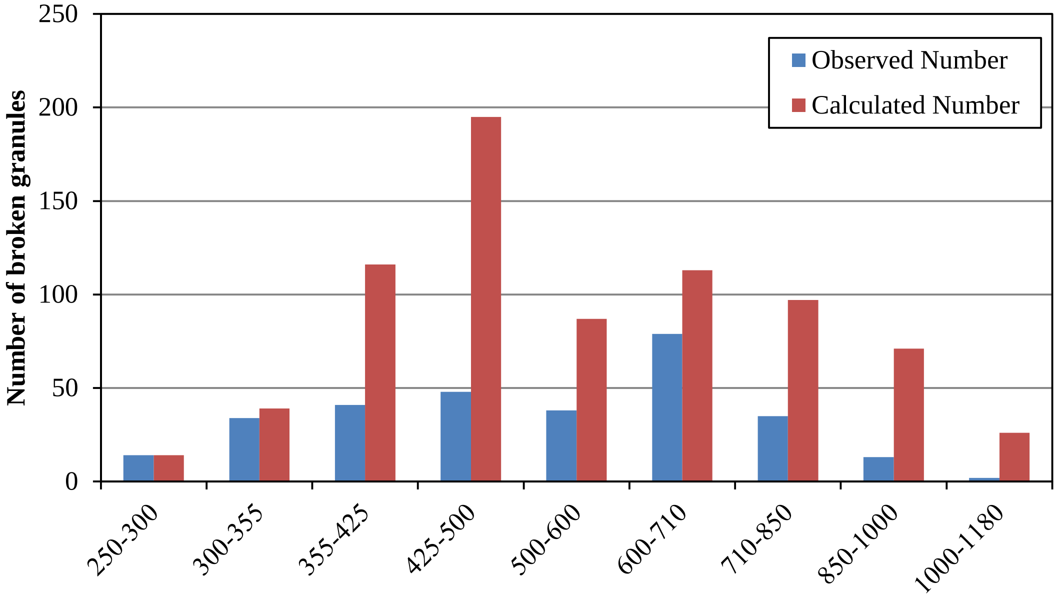


Figure 8. Comparison of results of number of broken granules obtained by two different methods

The estimated number percentage of particles in different sieve cuts for 45 g of feed material (before impact) is shown in Table 1. This has been obtained by converting the volume distribution to number distribution. If the number of broken granules is normalised in each sieve cut so that it is given per 10000 granules present in that sieve cut, then the results will look much different because of the presence of smaller numbers of larger granules, as shown in Figure 9. It is clearly indicating the prevalence of failure for the large granules.

Table 1. Number percentage of particles in different sieve cuts in 45 g of sample

Sieve Size Cut (µm)	**250-300**	**300-355**	**355-425**	**425-500**	**500-600**	**600-710**	**710-850**	**850-1000**	**1000-1180**
Number Percentage of Particles in 45 g of Sample (%)	**3.08**	**28.32**	**38.31**	**17.30**	**8.03**	**3.49**	**1.01**	**0.37**	**0.09**

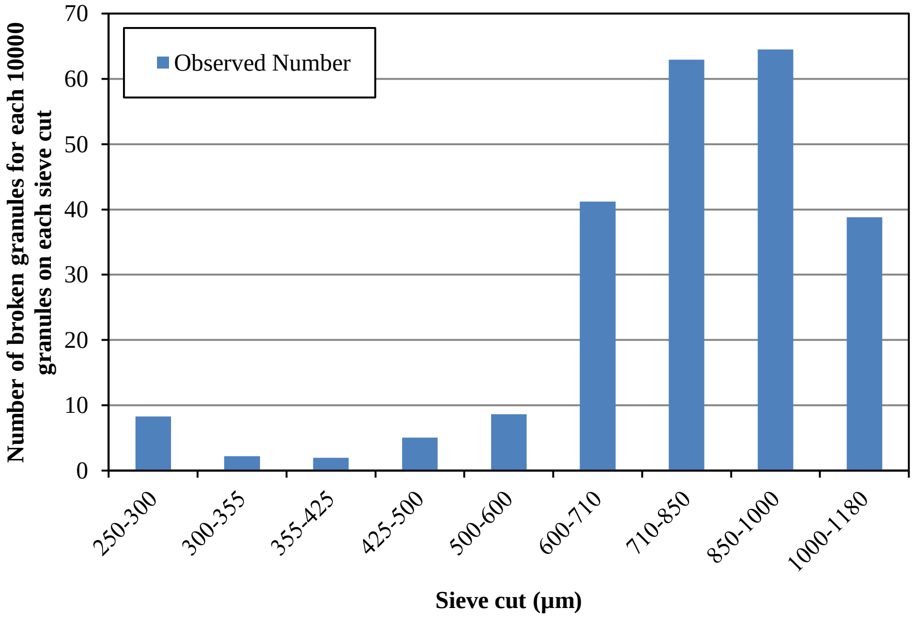
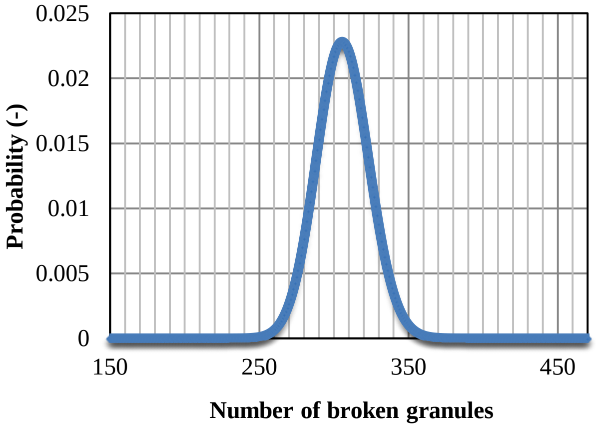


Figure 9. Comparison of results of broken granules for each 10000 granules on each sieve range, obtained by observed method

The probability of the broken granules as a function of the number of granules, based on the Poisson distribution, is shown in Figure 10 for the ‘observed’ method.



(a)

Figure 10. Probability distribution of broken granules based on the Poisson distribution for the observed number of broken granules

Considering the observed number of broken granules, there are 306 broken granules in 45 g (548,268 granules), corresponding to 0.056% by number. The coefficient of variation of the number of broken granules is 5.7 %.

The results presented above are based on 10 m/s impact velocity. This velocity was chosen to get a reasonable number of broken granules for counting and observation, and at the same time it represented a mid-range velocity in the air extraction ducts in a typical plant. However the impact velocity used in the PSI tester is 5 m/s. Therefore it is also of interest to explore and predict the trend of the results for the impact velocity that is relevant to the PSI tester.

Generally, the breakage of granules depends on the mode of failure. The extent of breakage for materials with a semi-brittle mode of failure can be found based on the model of Ghadiri and Zhang [29], Eq. (4).

$$W = \alpha \frac{\rho D H V^2}{K_c^2} \qquad \text{Eq. (4)}$$

where α is the proportionality factor, ρ is the envelope density of the particle, D is the particle average diameter and V is the impact velocity. H and K_c are hardness and fracture toughness of material, respectively. For the brittle mode of failure, the model of Vogel and Peukert [30] can be used to estimate the extent of breakage, as it is based on the Weibull distribution, and is shown in Eq. (5).

$$S = K f_{mat} x (mV^2 - W_{k,min}) \qquad \text{Eq. (5)}$$

where S is the breakage probability, f_{mat} is a material parameter, x is the particle size, mV^2 represents the kinetic energy and $W_{k,min}$ is the minimum kinetic energy which causes breakage.

Based on the equations above, the extent of breakage is a function of the square of impact velocity, V^2. Therefore if the impact velocity is reduced from 10 m/s to 5 m/s, a four-fold reduction in the number of broken granules is expected. Based on the new number of broken granules the new coefficient of variation is calculated. The results are shown in Table 2.

Table 2. Dependency of the broken number of granules on the impact velocity

	Observed Number of Broken granules
Number of Broken granules in 45 g and (Number %) at 10 m/s	306 (0.056%)
CV (%) for Impact at 10 m/s	5.71
Number of Broken granules in 45 g and (Number %) at 5 m/s	76 (0.014%)
CV (%) for Impact at 5 m/s	11.44

The CV increases as the impact velocity is decreased. Based on these results, the largest value of CV is around 11% based on material characteristics and 5 m/s impact velocity. This is much lower than those achieved by the current test devices. Therefore modifications and improvements of the devices would help to decrease the CV to approach the actual CV of the material itself.

4. CONCLUSIONS

Single particle impact testing of placebo enzyme granules was carried out to identify if there were outliers amongst the granules in terms of their impact strength and to quantify their numbers. The Poisson distribution was applied to describe the Coefficient of Variation of the number of broken granules. A minimum CV of around 6% was obtained for an impact at 10 m/s, using a granule mass of 45 g. The CV would change for other masses and impact velocities. Increasing these two variables would decrease the CV. For both brittle and semi-brittle failure of the granules the probability of breakage is a function of the square of the impact velocity. So it is possible to estimate the number of broken granules at different impact velocities. For impact testing at 5 m/s the results show 11% as a value for the CV. This is the minimum CV that is possible to get for 45 g mass tested at this velocity, and is limited by the material characteristics. It can be used as a benchmark to compare the performance of test devices.

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REFERENCES

1. Palmer, T. (2001). Enzymes: Biochemistry, Biotechnology and Clinical Chemistry, 1st Edition, Horwood Publishing Ltd.

2. Pepys J., Hargreave F.E. and Longbottom L.J. (1969). Allergic reactions of the lungs to enzymes of Bacillus subtilis. Lancet; 1, 1181–1184.

3. Flindt, M.L.H. (1969). Pulmonary disease due to inhalation of derivatives of bacillus subtilis containing proteolytic enzyme. Lancet, 1, 1177–81.

4. Sarlo, K., Fletcher, E.R. and Gaines, W.G.(1997). Respiratory Allergenicity of Detergent Enzymes in the Guinea Pig Intratracheal Test: Association with Sensitization of Occupationally Exposed Individuals. Fundam Appl Toxicol, 39, 44–52.

5. Vanhanen, M., Tuomi, T., Tiikkainen, U., Tupasela, O., Voutilainen, R. and Nordman, H. (1999). Risk of enzyme allergy in the detergent industry. Occup Environ Med, 57, 121–125.

6. AISE: Guiding principles for the safe handling of enzymes in detergent manufacture, AISE document.

7. Bruce, C.F., Dunn, E., Brotherton, R., Davies, D.R., Hall, R. and Potts, S.C.M. (1978). Methods of Measuring Biologically Active Enzyme Dust in the Environmental Air of Detergent Factories. The Annuals of Occupational Hygiene, 21, 1-20.

8. Heubach GmbH. (2005). http:/www.heubachinternational.de.

9. Ahmadian, H. (2008). Analysis of Enzyme Dust Formation in Detergent Manufacturing Plant. PhD Thesis, The University of Leeds.

10. Van Ee, J.H., Misset, O., Baas, E.J.(1997). Enzymes in Detergency, Surfactant Science Series; v. 69, 1st Edition, Marcel Dekker, New York.

11. Boerefijn, R., Gudde, N.J. and Ghadiri, M. (2000). A review of attrition of fluid cracking catalyst particles. Adv. Powder Technology. 11(2), 145–174.

12. Bentham, A.C., Kwan, C.C., Boerefijn, R. and Ghadiri, M. (2004). Fluidised-bed jet milling of pharmaceutical powders. Powder Technology, 141, 233-238.

13. McKay, A.T. (1932). Distribution of the Coefficient of Variation and the Extended “t” Distribution, Journal of the Royal Statistical Society; v. 95, 4th Edition, 695-698.

14. Yüregir, K.R., Ghadiri M., and Clift R. (1986). Observations on impact attrition of granular solids. Powder Technol., 49, 53-57.

15. Samimi, A., Ghadiri, M., Boerefijn, R., Groot, A. and Kohlus, R. (2003). Weibull Analysis of Quasi-Static Crushing Strength of Catalyst Particles. Powder Technology, 244, 130, 428-435.

16. Papadopoulos, D.G. (1998). Impact breakage of particulate solids. PhD thesis, University of Surrey.

17. Frye, L. and Peukert, W. (2004). Progress in the understanding of bulk solids attrition in dilute phase pneumatic conveying. Powder Technology, 143-144, 308-320.

18. Boerefijn, R., Ning, Z. and Ghadiri, M. (1998). Disintegration of weak lactose agglomerates for inhalation applications. International Journal of Pharmaceutics, 172(1-2), 199-209.

19. Cheong, Y.S., Salman, A.D. and Hounslow, M.J. (2003). Effect of impact angle and velocity on the fragment size distribution of glass spheres. Powder Technol., 138(2-3), 189-200.

20. Lecoq, O., Chouteau, N., Mebtoul, M., Large, J.-F. and Guigon, P. (2003). Fragmentation by high velocity impact on a target: a material grindability test. Powder Technology, 105, 39-51.

21. Tomas, J., Schreier, M., Gröger, T. and Ehlers, S. (1999). Impact crushing of concrete for liberation and recycling. Powder Technology, 105, 39-51.

22. Khanal, M., Schubert, W. and Tomas, J. (2004). Ball impact and crack propagation – simulations of particle compound material. Granular Matter, 5, 177-184.

23. Salman, A.D., Biggs, C.A., Fu, J., Angyal, I., Szabo, M. and Hounslow, M.J. (2002a). An experimental investigation of particle fragmentation using single particle impact studies. Powder Technology. 128, 36-46.

24. Subero, J., and Ghadiri, M. (2001). Breakage Patterns of Agglomerates. Powder Technol., 120, 232-243.

25. Samimi, A., Moreno, R. and Ghadiri, M. (2004). Analysis of impact damage of agglomerates: effect of impact angle. Powder Technology, 143-144, 97-109.

26. Jørgensen, K., Bach, P., and Jensen, A.D. (2005). Impact and attrition shear breakage of enzyme granules and placebo particles-application to particle design and formulation. Powder Technology, 149, 157-167.

27. Bortkiewicz, L. (1898). The law of small numbers. B. G. Teubner, Leipzig, Germany. (en.wikipedia.org/wiki/Poisson_distribution).

28. Rawle, A.F., (2014). http://www.thm.de/ibva/images/stories/doku/mastersizer/mrk456-01.pdf

29. Ghadiri, M., and Zhang, Z. (2002). Impact attrition of particulate solids. Part 1: A theoretical model of chipping. Chemical Engineering Science, vol. 57, pp. 3659-3669.

30. Vogel, L. and Peukert, W. (2003). Breakage behaviour of different materials – construction of a mastercurve for the breakage probability. Powder Technology, vol. 129, pp. 101-110.