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DRY MIXING OF SPICE POWDERS

INVESTIGATION OF EFFECT OF POWDER PROPERTIES ON MIXTURE QUALITY OF BINARY POWDER MIXTURES

A thesis submitted in fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

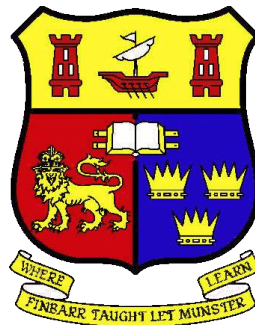
in

PROCESS & CHEMICAL ENGINEERING

at

THE NATIONAL UNIVERSITY OF IRELAND

UNIVERSITY COLLEGE CORK



By

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Under the direction and supervision of

Prof. Dr. Lilia Ahrne

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OCTOBER 2014

DECLARATION

This thesis is submitted by the undersigned to the National University of Ireland, University College Cork, for examination in the degree of Doctor of Philosophy (Process and Chemical Engineering). This thesis has not been submitted for any other degree (purpose) at this or any other university. The material presented in the thesis comprises entirely of my original work except where duly acknowledged. This document was written and compiled by me with editorial advice from Prof. Lilia Ahrne and Dr. John Fitzpatrick.

A handwritten signature in black ink, reading "J. Shenoy", is positioned above a horizontal dotted line.

To Amma, Papa, Pittu and Karthik- for their wholehearted love!

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Pursuing a PhD is like how someone famously wise once said “Expect problems and eat them for breakfast”. No matter how foolproof plans are, there are always issues, challenges and mysterious mishaps at each step, but once you face them head on and accept them, then the ride is more predictable and enjoyable. Many people have been part of this journey of my life and I would like to thank each one of them.

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PUBLICATIONS AND PRESENTATIONS

The following is a list of publications that were made in association with this work and have been published and submitted.

Publications

Shenoy, P., Innings, F., Lilliebjelke, T., Jonsson, C., Fitzpatrick, J., Ahrne, L. 2014. Investigation of the application of digital colour imaging to assess the mixture quality of binary food powder mixes. *Journal of Food Engineering*, 128, 140-145.

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CHAPTER 1

INTRODUCTION

1.1 Background

Mixing is a fundamental operation that has been used in different types of industries. It can be broadly categorized into mixing of liquids, solids or gases. Mixing is done to manufacture products with consistent product properties and to reduce the gradients in composition, colour, taste or texture. Although mixing process appears to be a simple operation, in reality it is quite complex in nature. Dry mixing that uses only particulate solids is most difficult to understand due to the dynamic nature of the solids and the differences in properties such as particle size and shape in the same solid especially for food powders.

The final mixture quality of the product is extremely important for the manufacturers as it can directly influence the functionality of their products. To control product quality it is important to understand the mixing process and optimize the operating conditions. Powder properties are also important factors that influence final mixture quality of the product. A good mixture quality helps in reducing gradients in the final product such as taste, colour and texture; to have nutritionally balanced powder mixtures; to provide uniformities in mixing and to deliver product with uniform properties. The costs of failure to produce a high quality powder mixture are very high in all industries that use powders as a final or intermediate product. In the case of pharmaceutical industry where the rules and demands for final performance of product are more stringent this is a serious issue. Many industries still use trial and error methods to determine good mixture quality. Therefore, industries are increasingly paying more attention to understand the significance of the mixing process and the role of powder properties on the final manufactured product and apply methods to control the quality at early stages of manufacturing instead of post-production. By doing so, they are able to avoid wastage of resources, energy and also save money.

To design a multicomponent powder formulation and optimize the processing conditions for mixing is a complex task and requires knowledge about powder properties, interaction between particles during mixing, equipment characteristics as well as efficient methods to quantify and follow up mixture quality (MQ). Better knowledge about these will allow faster product development, higher consistency in quality of the final product, as well as possibilities to design improved mixing equipment.

The assessment of mixture quality is one of the most significant steps in the industry as it determines a critical quality parameter of the manufactured product. Previous studies (Muzzio et al, 1997) have discussed about the traditionally used thief probe sampling method and its limitations for analysis of mixture quality and current studies are focused more towards image analysis techniques that use statistical analysis. Keeping the industrial aspect in mind, in this project, the aim was to test the traditionally used conductivity method as well as a novel colour imaging based method which is simpler and faster compared to image analysis to analyse mixture quality of spice mixtures and to compare the benefits and deficiencies of each method. Coefficient of Variation (CoV) which is a commonly used index of MQ used by industries was used to assess the MQ as good or bad based on a threshold CoV value. Various studies (Bridgwater, 1976; Barbosa-Cánovas et al., 2005c; Nienow et al., 1997) have also tried to understand the role of particle size and density on the effect of powder MQ and segregation, but unfortunately not much work has been done using real food powders such as spices. While it is not easy to predict the mixing behaviour of powders with controlled properties, the behaviour of food powders is all the more difficult to predict since they also have a particle size distribution for the same powder. Each type of powder also has different grain size and shape. A spice mixture often consists of multiple ingredients required in a certain proportion to get the required taste and have a palatable appearance. Therefore, it is not possible to control the size range of the powders. Although it is proposed to minimize particle size and density difference in powders to avoid segregation this is not practical in a powder mixture. Therefore, in this work real spice powders have been used with a particle size range and which have different shapes and textures. Most studies (Kuakpetoon et al., 2001) have focussed on the use of tumbler mixer to conduct trials due to ease of sampling and to create modelling

solutions. Studies have not used convective mixers due to the difficulties with sampling. However, convective mixers are most commonly used by industries for powder mixing due to its faster mixing time and ability to handle versatile powder types. Thus, clearly there is a need to investigate the behaviour of food powders using convective mixers. In this study, a prototype paddle mixer has been used to conduct the mixing trials. This mixer has not been used for lab-scale mixing trials previously and has mostly only been mentioned in literature for its mixing mechanisms.

1.2 Objectives

1.2.1 General

To understand the influence of powder properties and mixture parameters on the mixture quality of food powder mixtures using easy-to-use methods that can effectively evaluate the final mixture quality.

1.2.2 Specific Objectives

To investigate the use of digital colour imaging system (DCI) to analyse the mixture quality of binary spice powder mixtures.

To study the effect of powder composition and water content on the MQ of three different binary mixtures that varied in mixability.

To study the effect of differences in median particle size and powder densities on MQ of different binary mixtures.

To compare the evaluation of MQ of binary and ternary powder mixtures by using two methods – salt conductivity method and DCI method.

1.2.3 Dissertation Outline

The present dissertation has been organised in different chapters. The second chapter consists of a general literature review that explains the significance of mixing and discusses about different types of mixing mechanisms and mixers. It also provides a short review on the studies on mixing and discusses the effect of different powder properties such as size, density, flowability, moisture content and so on on the mixture quality of powder mixes.

Chapter 3 describes the salt conductivity method that has been used in Chapter 5, 6 and 7 of this study. Chapters 4, 5, 6 and 7 are publication based chapters and can be read individually as it has a literature review, materials, results, and discussion section and therefore are independent chapters. Chapter 4 and 5 have been published and Chapters 6 and 7 are submitted for publication.

Chapter 4 is based on the paper 'Investigation of the application of digital colour imaging to assess the mixture quality of binary food powder mixes' which has been published in Journal of Food Engineering. Here the application of a digital colour imaging system known as DigiEye was studied to evaluate mixture quality of hand mixed binary spice mixtures.

Chapter 5 is based on the paper 'Dry Mixing of Food Powders: Effect of water content and composition on mixture quality of binary mixtures' which has been accepted in Journal of Food Engineering. In this study, the binary mixtures were mixed with different powder content ratios to check if this can influence the MQ of mixtures that have extreme differences in their ability to mix. Two mixtures that were expected to mix well - paprika:salt and sugar:salt mixtures and oregano:salt mixture that was expected to mix poorly were produced by mixing them in the paddle mixer and checking their mixture quality at definite time intervals. Different ratios were produced in the range of 20-80% salt. Trials were also conducted for trace amounts of salt. Trace quantities were used since industries sometimes add a component in minute amounts and usually disperse it by spraying it in the form of oil solution or mix it as a pre mix and add it to the final mix. In this study as liquid was not used for the trials the trace component salt was added inside the mixer along with the other powder. The influence of water content of paprika and oregano on MQ was investigated by conditioning them at different humidities and mixing with salt that was maintained at 30% relative humidity.

Chapter 6 is based on the paper 'Effect of powder densities, particle size and shape on mixture quality of binary food powder mixtures' that is submitted for publication. In this study different types of binary powder mixtures which had differences in median particle size and powder densities were mixed at equal quantities by weight, and mixture quality was analysed. The size ratios were varied in the range of 1.96 up to 15.73 to understand the range up to which the mixing behaviour of powders is not

affected. Powders with similar size and differences in bulk density were also studied to check if bulk density has a major impact on the mixture quality.

In Chapter 7, the digital colour imaging method and salt conductivity method discussed in chapters 3 and 4 in this study were applied to analyse mixture quality of both binary as well as quaternary mixtures produced in the paddle mixer. This chapter discusses the advantages and limitations of using these methods for evaluating the MQ of powder mixtures and provides a good overview of which method to use for a certain kind of mixture.

Finally chapter 8 discusses the overall conclusions in this work and suggests future recommendations in the field of study.

CHAPTER 2

LITERATURE REVIEW

2.1 Herbs, Spices & Their Mixes

Spices, flavourings and seasonings have been widely used to improve taste and flavour of food products. Spices contain essential oils and add aroma, piquancy, colour and distinctive flavour to food (Belitz, 2009; Ilyas, 1976). Some spices and herbs are also used for the preservation of food and are said to contain medicinal properties (Brown, 2008; Carlsen, 2011). Spices are aromatic by nature with the aroma originating from the root (onion, ginger, and garlic) and bark such as cinnamon or berry (black pepper) of herbaceous plants. Herbs are the leaf portions of plants, some examples of commonly used herbs are rosemary, thyme, basil and oregano (Brown, 2008). Since time immemorial man has used spices for health benefits. Turmeric a golden coloured spice is widely used in the Indian subcontinent and since the Ayurveda period(1900BC) and is recommended for its therapeutic properties such as treatment of skin, pulmonary, and gastrointestinal systems, aches, pains, wounds and other related disorders. Apart from the health benefits that it possesses it also helps in preserving food through its antioxidant mechanisms, provides colour to food and also adds taste (Aggarwal, 2007; Suresh, 2009). Red pepper is the most cultivated spice in the world and cumin is another spice commonly used in many food preparations (Ani, 2006; Cremer, 2000). Food companies commonly use spices in their ground state in the form of powder or dehydrated state (particulate form) except when using herbs which are mostly never powdered in order to preserve its appeal to customers. Spice powders are usually added to other foods. The manufacture of spices in powder form helps lower the water activity in the spice which in turn prevents microbial spoilage and helps in increasing the shelf life of the product. Producing food in a powder form also helps in reducing the transportation costs since it is easier to store (Fitzpatrick and Ahrne, 2005). With increase in demand for novel flavors and exotic tastes, companies that manufacture flavorings, seasonings and food mixes are forced to continually develop and test a variety of recipes that consist of multiple ingredients. A quick glance at the supermarket

shelves would show how almost every vegetable, nut or fruit is manufactured in its dehydrated or powdered form. There are also plenty of ready to make foods in the form of powder mixes such as macaron and cake batter mixes, powdered alcohol, potato flour, icing sugar, instant coffee mixes, ready to make chutney powder mix, powdered candies, soup mixes and so on.

Dehydrated powders such as potato powders are very popular amongst the consumers due to their ease of use and are especially attractive for companies as they can be sold in the form of raw powder, semi-finished or finished product consumed as baby food or as food for the elderly (Carillo et al., 2012). A large group of flavour components that are added in spice and juice mixes such as protein broths, vinegar powders, soy powders and dehydrated fruit bits and powders, are spray dried powders (Brown, 2008). Although all the properties used to characterize powders can be applied to food powders it may be difficult to analyse spice powders, herbs, and other food powders since they are organic in nature and therefore may affect the predictability of some of its properties. Thus, optimizing and updating knowledge in powder technology is of critical importance to the food industry.

2.2 Mixing

2.2.1 Mixing Process

Mixing of solids is a universal technique where one component gets dispersed with another component. In case of powders, it is influenced by different powder properties such as grain size, shape and particle size distribution. Mixing mechanisms of powders are not sufficiently known and in most cases it is difficult to obtain an 'ideal mix'. Therefore, random mixing is more commonly observed (Sommer, 2000).

Dry mixing is a process that is widely used in many kinds of industries such as manufacture of ceramics, plastics, fertilizers, detergents, pharmaceuticals and food & animal feeds (Fan et al., 1990). Mixing is an important step for the food industry to produce products with consistent properties and obtain uniformity in different properties such as color, texture, taste and concentration. The objectives of the mixing can be different based on the application of the product; in some cases it may be performed when the materials being mixed should chemically react with one another whereas in other cases it can be to help alter the mechanical properties of the final

product by changing the spatial configuration of the particles (Lacey, 1943). Most of the food mixing processes industrially used are batch operated, as the costs for installation are low. A good mixing process should be able to produce a uniform mixture with minimum overhead costs, power, labor and minimum time (Barbosa-Cánovas et al., 2005b).

Mixing can be performed for components in any phase: solid, liquid or gas. Mixing of fluids has been extensively researched for years. In the case of solid-solid mixing it is common to use trace amounts of solid in a liquid form and spray it into the process to mix it with the remaining solids. However, in this work we will focus only on solid-solid mixing using real food powders, i.e. not model systems or tracers. In fluid mixing, particles are of a molecular size and possess intrinsic mobility, which makes it possible to achieve an almost perfect mixture. However, in the case of solid-solid mixing they do not possess such intrinsic mixing capability (Lacey, 1943) and during mixing there is a risk of segregation while or after mixing due to differences in particle characteristics (Nienow et al., 1997). The presence of cohesive powders can inhibit such actions but can also be a contributor to improve the mixture quality.

2.2.2 Challenges in mixing of solids

Food powders are complex to study and what makes it even more challenging is that the properties and movement of the powder can change during the mixing process (Barbosa-Cánovas et al., 2005c; Berk, 2008). Dry powder mixing poses many challenges by affecting the final product state and therefore more research is needed to thoroughly understand the underlying concept. To study the powder mixing mechanism it is important to understand the effect of primary powder properties such as powder density, shape, particle size etc. (Barbosa-Cánovas et al., 2005a).

Important factors that need to be considered while mixing different types of powders are: a) type of mixer selected, b) characterization of the resultant mixture state, c) rate and mechanism of the mixing process (Fan et al., 1990) and d) powder properties.

2.2.3 Types of Mixtures

An ideal mixture is the one in which at any point of use it matches product specifications. According to Barbosa-Cánovas, G.V. et al (2005b) mixtures can be divided into three categories :

- i. Random (non- interactive)
- ii. Ordered (interactive)
- iii. Segregating

i. Random mixtures

When powders that do not differ in their physical properties and possess freedom of movement are mixed together, they form a non-interactive random mixture (Figure 2.1). In such mixtures the chances of finding a particle component across any point of the mixture is same irrespective of the neighbouring particles (Barbosa-Cánovas et al., 2005b; Muzzio et al., 2004).

ii. Ordered mixtures

In case of cohesive powders the segregation tendency is reduced because it is difficult to separate the attached particles from one component and mix them with particles of another component. Here the inter-particulate bonding mechanism tends to make the particles move in an associated manner as shown in Figure 2.2 (Fan et al., 1990; Barbosa-Cánovas et al, 2005b). For cohesive systems, surface forces cause the sticking of small or very fine particles (less than 5 μ m) (referred as guest particles) onto the surface of a larger particle (referred as the host particle)(Muzzio et al., 2004). Thus samples taken from any point in this system will be identical in nature. The fine particles have strong inter-particle forces between them that are formed due to moisture, electrostatic charging and van der Waals forces (Barbosa-Cánovas et al., 2005b).

iii. Segregating mixtures

When free-flowing powders are mixed together, due to the presence of independent mobility amongst the particles, it tends to become segregating in nature as shown in Figure 2.1 (Barbosa-Cánovas et al, 2005b). In these mixtures, it is very difficult to achieve a good mixture quality. For some powders it can be tough to mix them or to maintain good mixture state due to extreme differences in their particle properties. Size

difference has been reported as one of the main reasons that causes segregation (Nienow et al., 1997). According to Muzzio et al (2004) although segregation is more commonly observed in free flowing mixtures it can also be present in cohesive mixtures where segregation of ordered units with different sized carrier particles or leftover adherent particles is a possibility.

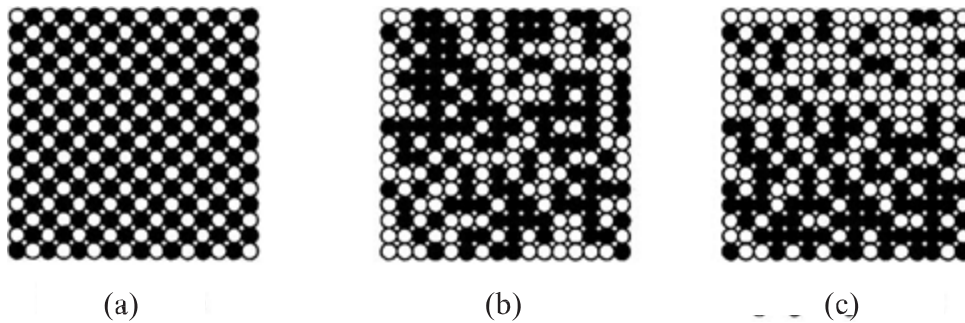


Figure 2.1- a) Perfect mixture b) Random mixture c) Segregating mixture (reproduced from Barbosa-Cánovas et al., 2005b; Rhodes, 2008)



Figure 2.2- Fine particles adhered to carrier particles (Barbosa-Cánovas et al., 2005b)

2.2.4 Different types of mixing mechanisms

Mixing of particles is a reversible process in which the particles in action change their path of circulation. When two particles exchange their positions, proper mixing does not take place hence it is preferred that particles possess different circulation paths to

obtain a good mixture. The three main mechanisms involved in mixing of solids are discussed below.

Convective

In this type of mixing, there is a mass movement of particles from one point to another; this could be caused by motion of a stirring device in the vessel (Muzzio et al., 2004). Bulk powder mixtures are mixed macroscopically where microscopic scale level mixing changes cannot be expected. Therefore even though the final mixture appears to be good, at a fine level the mixing quality can be poor for pure convective mixing. E.g. trough mixer with a ribbon spiral (Barbosa-Cánovas et al., 2005b).

Diffusive

It is also known as random walk phenomenon as individual powder particles move in a random manner. It is similar to Brownian motion of molecules in fluids. Pure diffusion is a slow mixing process which is highly effective. E.g. Tumbler mixer.

Shear

This mixing is caused by the exchange of momentum between powder particles caused by the formation of slipping of planes in the bulk material. It promotes semi-microscopic mixing and is beneficial in both batch and continuous operation. E.g. it can take place near agitating impeller, rotary vessel mixers (Barbosa-Cánovas et al., 2005c).

2.2.5 Types of Mixing Equipment

Mixing equipment can be divided into four major types (Fan et al., 1990):

Tumbler

In this type of mixer, a totally enclosed vessel is rotated about an axis and it is mounted on a shaft with support from bearings. The particles are mixed by tumbling them. Free-flowing non-segregating powders can be used in this type of mixer. Tumbler mixers can be further classified depending on their varied forms.

- a) Horizontal cylinder
- b) Double cone blender
- c) V-cone
- d) Y-cone blender (Barbosa-Cánovas et al., 2005b)

Convective

Convective mixers are most commonly used in industrial applications and ribbon blender is one of the common general purpose mixers (Figure 2.3). Other mixers include the paddle mixer, Nauta mixer and Z-blade mixer. Paddle mixers promote rapid mixing of powders due to high powder mobility and are generally ten times faster than ribbon mixers. Both paddle and ribbon mixers promote mixing throughout the mixing chamber due to presence of its stirring device such as ribbons and paddle agitators that actively sweep the entire volume in the mixer (Harnby, 1997b; Muzzio et al., 2004). An advantage of convective mixers is that it can handle materials that can be prone to segregation or agglomeration due to its convective and shear mixing effects. For cohesive powders orbiting-type vertical screw mixer can be used (refer Figure 2.4).

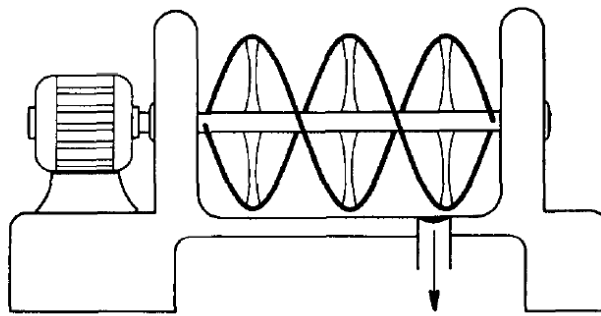


Figure 2.3- Ribbon blender (Fan et al., 1990)

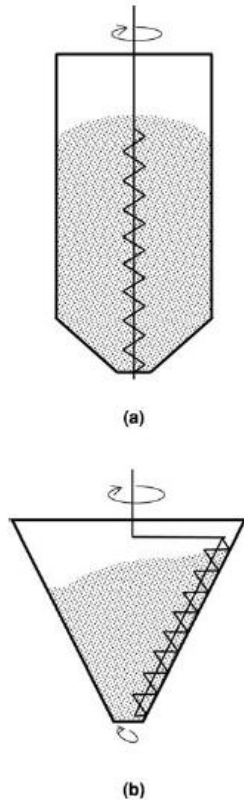


Figure 2.4- Mixer with vertical screws (reproduced from Barbosa-Cánovas et al., 2005b)

These are especially useful when mixing small quantities of powders into larger mass (Barbosa-Cánovas et al., 2005b).

Hopper (Gravity flow)

In this type of mixer the particles move under the influence of gravity and to prevent dead zones inside the mixer a central cone is used. If particles are recycled by mechanical or pneumatic means, axial mixing can be achieved. However, there is always a risk of percolation segregation in such mixers (Fan et al., 1990; Harnby, 1997b).

Fluidized Mixers

Here both gravity and convection currents are present (Figure 2.5). The gas stream flows in a direction opposite to that of force of gravity and the turbulence caused provides excellent mixing of the particles (Fan et al., 1990).

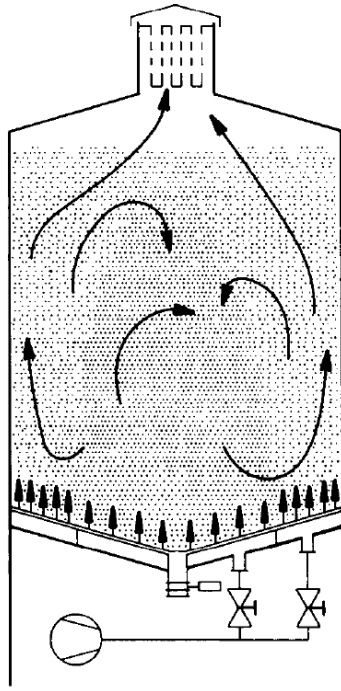


Figure 2.5- Fluidised bed (Fan et al., 1990)

Characteristic curve for mixing process

The characteristic curve of mixing is useful to evaluate the performance of mixers. It depicts the stages of mixing when powder mixing takes place. When the degree of mixedness (M) is plotted on a logarithmic scale against mixing time, the characteristic curve for mixing is obtained. In a batch operation, the mixing time is the time from the start of mixing whereas in a continuous operation it is the measure of the mean residence time of the powder. The curve shown in Figure 2.6 shows convective mixing in the first stage and it is then followed by a mix of convective and shear, and later ends with a diffusive type of mixing to achieve a final state of mixedness M_{∞} . The factors that influence are mainly operating conditions and the powder properties (Barbosa-Cánovas et al, 2005b).

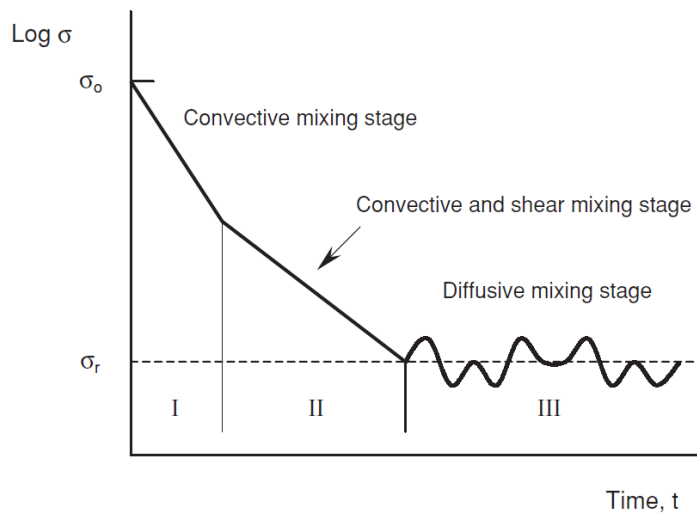


Figure 2.6- Characteristic curve of mixing (Barbosa-Cánovas et al., 2005b)

2.3 Segregation or Demixing

2.3.1 Over mixing

When mixers are operated for longer duration than required they cause more damage to the products being mixed instead of actually helping in bringing about a homogenous mixture (Nienow et al., 1997). Powders being dynamic in nature require an optimal mixing time, energy and frequency, when this is above or below the optimal limit it causes the ingredients of the mix to segregate or to be cohesive in nature. In some cases it may also lead to breakage of brittle particles. Thus improper mixing can cause mixing and demixing at the same time inside a mixer (Berk, 2008). Therefore it is important to not over mix the powders by setting a threshold or a limit in its mixing time.

2.3.2 Segregation

The reverse mechanism of mixing is known as segregation. Segregation is usually caused when particles with different sizes, shapes, densities, moisture content, friability, flow properties and agglomeration tendencies are used for mixing. It can also take place when particle motion causes electrostatic charging inside the mixer. Segregation of powders is a serious issue that can cause functional or nutritional problems in a product when low concentration components tend to segregate from the mixture. For example segregation of vitamins from infant formula or segregation of baking powder from

dessert mixes can completely make the product unusable or undesirable. Cohesive powders show a lower tendency to segregate as they have the capability to form ‘ordered’ mixtures due to the adherence of fines to larger particles (Barbosa-Cánovas et al., 2005e). The three main segregation mechanisms (Barbosa-Cánovas et al., 2005e; Rhodes, 2008) are as follows and have been shown in Figure 2.7:

- a) Trajectory segregation
- b) Percolation segregation or Rolling Heap Mechanism
- c) Upthrusting

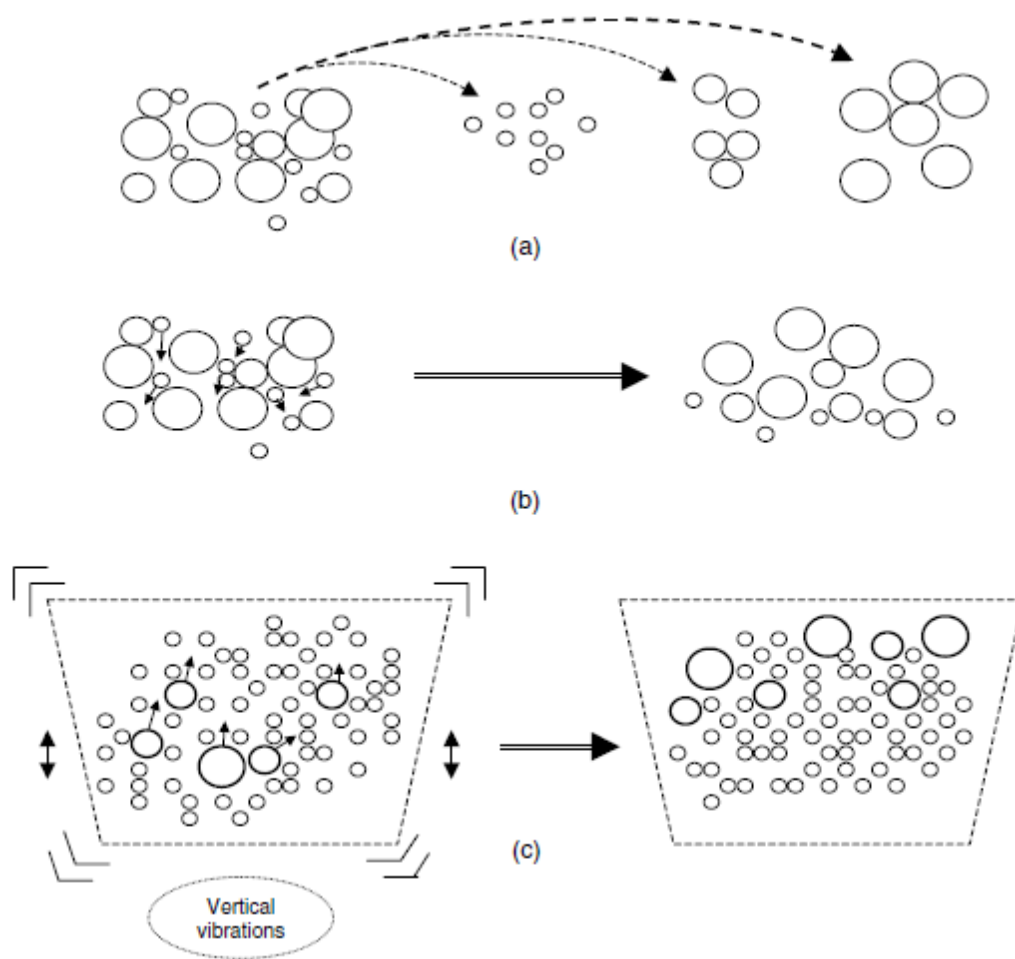


Figure 2.7- Segregation Mechanisms a) Trajectory segregation b) Percolation Segregation c) Upthrusting (Barbosa-Cánovas et al., 2005e)

In trajectory segregation, particles with different sizes and densities have different velocities that determine the horizontal distance that they can travel on exerting the

force to mix them. In the case of commonly observed percolation mechanism, in a mixture of particles with different sizes the smaller particles percolate through the voids created by larger particles and fall downwards. This kind of segregation can arise due to vibration, motion or gravity. A common way to check if a mixture containing particles with different particle sizes can segregate is to pour the mixture through a funnel and check the outer edges and inner core of the heap for a change in particle size distribution (Figure 2.8). Upthrusting is the phenomenon where the larger particle moves upward from a bed of fine particles and this can take place even if the larger particle is denser than the fines.

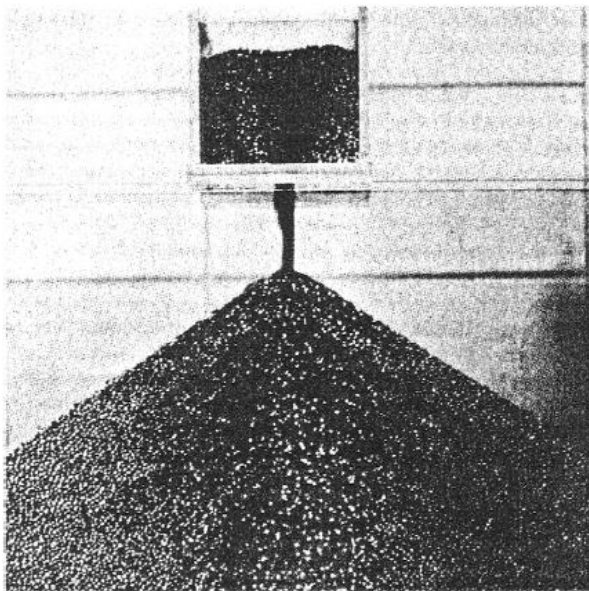


Figure 2.8- Heap test for multi-sized particles (reproduced from Nienow et al., 1997)

In order to produce good quality powder mixes and avoid segregation between the different ingredients of a powder mix it is very important to minimize the differences in particle size of various ingredients used in the mix. Particle Size Distribution of the individual ingredients is a key attribute for evaluating a powder mix homogeneity (Chowhan, 1979). Most of the soup and soft drink mix manufacturers usually sell their mixes in small individual packets instead of selling mass quantities in large boxes. They also grind all the particles to the same size in order to avoid size segregation issues as

they generally need to use different sized particle ingredients to produce their products (Kaye, 1997).

2.4 Mixture Quality and it's Assessment

2.4.1 Mixture Quality

Mixture quality refers to the homogeneity of mixture components throughout the whole of the mix. It is commonly assessed by taking samples from different parts of the powder mixture, measuring the concentration of a component within each sample and evaluating an index of the deviation of these concentrations with the component concentration in the mixture recipe. Lower deviation produces better mixture quality. Commonly used indices of mixture quality are sample variance / standard deviation and coefficient of variation (also known as relative standard deviation). There are many factors that influence the assessment of mixture quality, including the sampling methodology and the techniques used to measure component concentration or variables that are related to component concentration, such as salt conductivity, colour and near infra-red radiation.

2.4.2 Sampling

Sampling is a crucial step for mixture quality evaluation, which requires planning and analysis before implementation. It consists of taking small amounts of samples in mass or volume units from different locations in the mixer. Some of the known 'golden rules' that have to be followed during sampling are:

- 1) To take samples from a moving stream: In case of batch mixing operations it is advised to take the samples after mixture discharge however in many cases sampling is done inside the mixer on the stationery powder bed when samples are withdrawn after fixed time periods.
- 2) To take samples randomly across the entire section of the powder bed: Imagine a vertically segregated powder bed; in such a case it is not good to do sampling only on the top or bottom surface of the powder bed as this would provide incorrect results of the state of mixture quality (Fitzpatrick, 2009; Harnby, 1997a).

The sample size selected should represent the mixture quality of the whole mixture. The mixture quality determined depends on numerous factors such as:

- a) The size of the sample used
- b) The number of samples taken
- c) The position from which the sample is taken
- d) The sampling method used

Sample size

The smallest sample size for a mixture is that of the size of the smallest particle in the mixture. Similarly the largest sample size for a mixture is to consider the whole mix. Thus the choice of sample size depends on the application of the final product, in case of pharmaceutical products it can be a tablet or a capsule, in case of instant coffee drinks the sample size is equal to a sachet that can be 50g or 25g by weight, and in some cases it can be as high as a whole bag weighing 25 kilos. Thus in order to determine a relevant sample size or scale of scrutiny the consumer needs has to be taken into consideration (Fitzpatrick, 2009). It is recommended to have a sample size greater than the amount required for the analytical technique (Manjunath et al., 2004). In case of food powders it can be difficult to obtain perfect unbiased samples from the main mixture due to the heterogeneous nature of the powders (Barbosa-Cánovas et al., 2005d).

Number of samples

The number of samples directly affects the variance of the measured mixture quality. When the number of samples is small, the variance is very high and as the number of samples is increased the variance reduces (Fitzpatrick, 2009). Literature suggests that at least 15 to 30 samples should be taken to make a proper analysis of the mixture quality however this is often impractical and in reality only 10 or 20 samples are withdrawn due to physical constraints (Manjunath et al., 2004; Muzzio et al., 1997). According to Manjunath et al (2004), as a rule of thumb the total amount of sample withdrawn from a batch mixer should not be greater than 5% of the charge.

Sample location

The location of the sample is an important parameter while sampling. Care must be taken to choose locations that can cover all the random spots of the mixer. In a random sampling process the chances for a member to be sampled again is the same (Barbosa-Cánovas et al., 2005d).

Sampling methods

A thief probe is commonly used to withdraw samples from stationery powder beds. There are different types of thief probes such as side-sampling or slot sampler thief probe or end sampling thief probe. This method is very easy to practice and is most preferred by the industry. However it can provide biased information due to the sampling or analytical error. When the probe is inserted into the powder bed it disturbs the original state of the powder bed. Particles in the path of insertion enter into the thief probe and therefore the particles that are actually withdrawn and used for analysis from the cavity of the thief probe may consist of these dragged particles of different sizes and this introduces an error in the analysis (Manjunath et al., 2004; Muzzio et al., 1997).

2.4.3 Sample Variance and Coefficient of Variation

The sample variance and the coefficient of variation are often used as measures of mixture quality. The sample variance (S^2) is calculated as shown in equation 1. The lower the sample variance is the better the mixture quality will be. Often Relative standard deviation(RSD) or Coefficient of Variation (CoV) (equation 2) is used as a measure of mixture quality especially by the pharmaceutical companies (Fitzpatrick, 2009). CoV takes into account the influence of composition unlike standard deviation (S) and therefore is more suitable (Williams, 1968). Detailed information about sampling method and calculations used in this study is discussed in chapter 3.

$$S^2 = \frac{\sum_{i=1}^N (y_i - \mu)^2}{N} \quad (1)$$

Where y_i is the composition of component in sample i , μ is the mean composition or composition of the component in the whole mix and N is the number of samples.

$$\text{CoV} = \frac{S}{\mu} \quad (2)$$

Companies require sampling and analysis techniques which are easy to implement and not time consuming and hence the method used for sampling and measuring the mixture quality are chosen based on the final application of the product.

2.5 Image analysis and Colour techniques for Assessing Mixture Quality

2.5.1 Image Analysis Techniques

The quest for alternative and more effective non-destructive methods for analysis of mixture quality by researchers led to the use of image analysis to measure the mixing efficiency (Muerza, 2002). In a study by Berthiaux et al (2006) homogeneity in powder mixing was evaluated by use of principal component analysis (PCA) technique. The images captured were digitized so that a grey scale image containing the information of tracer concentration could be obtained. The diameter of any particle studied was equal to 5 pixels and the images captured were quantized and divided into L number of rectangular areas on which the PCA analysis was done by checking the concentration of solids in the stream to determine the homogeneity in the sample. A mixture was considered as homogeneous if the composition and properties for a test element was same as that of rest of the elements . Only the main principal components (where maximum variability is observed) is considered for analysis (Berthiaux, 2006).

Daumann et al (2008) used image analysis to study the mixing efficiency of solid mixtures in a single shaft mixer. Products with different colors and different particle sizes were used. While mixing the image was taken using the Sony VX 2100E camera and image analysis was done using the Image J (open source program) software. This software transformed the different particle fractions into a black and white binary image and from the image the total surface area of individual particle fractions were obtained by counting the pixels occupied by each size. The result of the mixing efficiency calculated from the image analysis was compared with sieving result and it was seen that both curves were similar except for some error due to sampling. Through this work it was concluded that it was possible to measure the efficiency of mixing through image analysis for the surface of the mixture but it was not possible to find the local distribution of the particles as similar coloured particles were considered to be one unit by the software. The authors suggested that the method cannot represent the mixing efficiency of the whole mixture but by using a tracer one can observe the mixing

behavior (Daumann, 2008). Daumann et al (2009) also reported using image analysis and statistical methods to evaluate mixture quality of cement and ultramarine blue after mixing it in a 120L twin paddle mixer (Daumann, 2009). Several other studies also reported using image analysis followed by different types of statistical analysis to measure the mixture homogeneity (Aissa et al., 2010a; Le Coent, 2005; Van Puyvelde, 1999).

As discussed above, most of the image analysis techniques convert images into black and white form and this limits its application to only binary mixtures. To overcome this difficulty, in one study by Aissa et al (2010b) four linear medium density polyethylene (LMDPE) powders with similar properties and that were different only in the color were mixed in a rotating cylinder and analyzed using Red-Green-Blue (RGB) analysis. In this study the principle used was that the concentration of each particle type on the surface is equal to the initial composition of the mix before mixing. Color analysis was done using the multivariate image analysis. The color intensity of each pixel was transformed onto a lower dimensional plane and studied using PCA technique. With the help of the score vectors (t) the coordinates of each pixel on the new plane was obtained which helped to plot them as a two-dimensional score density histogram to improve the visualization of the color. All the pixels with similar t1-t2 combinations had similar color and were grouped together and brighter the colors were higher was the pixel density. On counting the number of pixels in each region it was able to identify the surface fractions of each color in the image. It was possible to follow the mixing state as a function of time and the signals from the RGB analysis stabilized with time on attaining equilibrium (Aissa et al., 2010b).

Though the method of image analysis has already been used on powders across various disciplines to study the mixture quality it is seen that not much work has been done on ternary or quaternary mixtures and most of the studies used binary black and white images and grey scale image analysis. Also these studies applied complex statistics to determine the mixture quality. In industries many number of powder products are manufactured daily and it is difficult to apply such time consuming techniques to evaluate if the product has obtained the desired mixture quality. In the work of this thesis the focus has been to apply industry friendly techniques namely colour analysis using an equipment known as DigiEye and salt conductivity based analysis and use

more commonly known indices such as variance and coefficient of variation. Colour analysis is increasingly gaining popularity and studies are being done to check how analysis of colour in the food product can help to control its quality or property changes. It will be interesting to extend the use of image analysis using L, a, b values on quaternary and even more complicated food powder mixtures which can be easily used and applied faster by industries to evaluate mixture quality of powder mixtures.

2.5.2 Evaluation of Colour

The quality of a product can be judged based on its colour. Consumers use colour to distinguish between any items of interest be it to buy fruits and vegetables or between two models of a car or between two different textile materials and colour can be the cause for acceptance of the product or for its rejection (Hunt. M.C., 1991). But the same colour perceived by one human being is perceived in a different manner by another individual; therefore colour interpretation is highly subjective. The factors that cause this are age, physiological factors and eye fatigue. Hence it is important to have a standard method which can be used to measure colour and assign it a numerical value. For this reason many instruments such as spectrophotometer, colourmeters and various colour spaces have been developed (X-rite, 2007). Some of the known colour systems are Munsell Colour system, HunterLab Colour system and CIELAB colour system. Of this the CIELAB is the most advanced colour space that was developed in 1976 compared to Hunter L,a,b that was developed in 1931 (CIE L* a* b* Color scale, 2008) and is also recommended by the CIE (Commission Internationale de l'Éclairage, 1986) (Laurent B. , 2007). CIELAB is expanded in the blue region and is mathematically derived from the X, Y, Z values. To see a colour the eyes need three things: an illuminant, an object and an observer (CIE L* a* b* Color scale, 2008; X-rite, 2007). The instruments used to measure colour use the wavelength reflected from that colour to form a reflectance curve (numerical value is obtained) and this can be mapped on to the colour space by the use of mathematics. The CIELAB system is based on the opponent colours theory which says that two colours cannot be both green and red at the same time (X-rite, 2007). In case of CIELAB, L* represents lightness for +values and darkness for – values, a* represents redness for + values and greenness for – values and b* represents yellowness for + values and blueness for – values (CIE L* a* b* Color scale, 2008) (Figure 2.9).

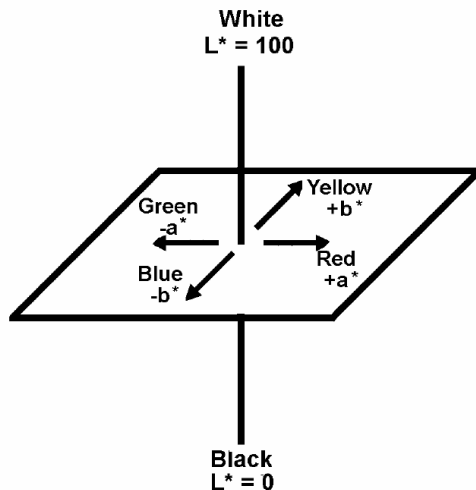


Figure 2.9- Color space for CIELAB (CIE L* a* b* Color scale, 2008)

To check the colour difference between two samples, it is useful to use the Delta E (ΔE) which takes into account L*, a* and b* and therefore gives a measure of the colour distance between the two samples (X-rite, 2007).

Colour evaluation is increasingly being used by food companies to study the quality of products or follow changes that take place during processing. It has been applied in meat industry to evaluate and follow the colour changes in meat after curing or meat processing. In another case the quality of tomato pastes imported by Nigerian food marketers was evaluated using colour measurements amongst the other techniques applied, to check if it was in agreement with the Food and Drug Administration standard requirements (Hunt. M.C., 1991; Sobowale, 2012). Colour assessment was used to determine the yellowness of bananas (Ji et al., 2013), to determine the maturity of mango (Jha et al., 2007) and to study the relationship between weight and surface gloss of eggplants (Jha et al., 2002). A 1 unit difference in the colour parameters suggests a colour difference that can be perceived by human eye.

In this project a commercially available digital colour imaging system known as DigiEye that uses CIELAB scale has been used to evaluate the mixture quality. More information on DigiEye equipment and its application is presented in chapter 4.

2.5.3 Alternative methods for evaluating mixture quality

Besides image and colour analysis techniques alternate techniques that are proposed to evaluate mixture homogeneity are the application of Near Infra-red spectroscopy (NIR) and Magnetic Resonance Imaging (MRI) (Berntsson, 2002; Sommier, 2001). In case of NIR method a fibre-optic probe is inserted into the sample and the spectra obtained provides the information of the properties of the powder. The advantage of this technique is that it can be applied offline as well as for in line monitoring of the powder mixing. By monitoring the shift of standard deviations with time during the mixing it is possible to reach conclusion about the mixing state (Berntsson, 2002).

2.6 Mixer Parameters and Mixture Quality

The type of mixer, the paddle geometry and the operating parameters such as rotational speed can influence the powder mixture quality (Barbosa-Cánovas et al., 2005b). Based on operation methods the mixers can be divided into mechanical agitation, pneumatic agitation and gravity type mixers. Examples of mixers that are based on mechanical agitation are tumbler mixer, rotating drum mixers and convective mixers. However as we already saw in section 2.2.3 although these mixers use mechanical agitation each one is more suitable for handling specific types of powders. Convective mixers such as ribbon mixer can handle both free flowing as well as slightly cohesive powders whereas paddle mixers such as Forberg mixer can handle versatile powders ranging from free-flowing, segregating, non-segregating and slightly cohesive to friable ones due to their short mixing times. Example of a pneumatic mixer is the fluidized bed mixer, which makes use of convection currents and handles products gently. Gravity mixers on the other hand rely on downward flow of material due to gravity (Durr).

Rotational speed is an important parameter and it can be decided based on the extent of agitation and thermal transfer required during mixing (Nienow et al., 1997). Studies by Aissa et al (2010b) showed that on increasing the rotational speed of the rotating cylinder containing powders with same properties except colour, the mixture quality was improved.

Mixing time is also another parameter that determines the mixture quality. Too less or too much mixing will also affect the mixture quality of the powders. Mixing time depends on the type of powders used, high cohesive powders require longer mixing

time as compared to low cohesive ones (Kuakpetoon et al., 2001) Besides these factors the amount of powders present inside the mixer can also affect the mixture quality of the powders.

2.7 Powder and Particle Properties and Mixture Quality

Powder properties such as particle size, density, shape and surface properties are some of the key factors that affect mixture quality of powders.

2.7.1 Particle size and shape

Physical properties such as particle size and density affect the mixing characteristics of powders (Barbosa-Cánovas et al., 2005b; Nienow et al., 1997). According to Mikli et al (2000) all technological properties of the powder such as bulk density, flowability etc. depend on the shape and size of the particles. Thus it can be seen that particle size is an important factor that affects the mixture quality and it is generally recommended to have same particle size in a mix to avoid segregation problems (Nienow et al., 1997).

For a particle to be considered as a powder its approximate median size should be less than 1mm. Particle sizes are measured using different units ; larger and coarse particles are often measured in centimeters or millimeters whereas fine particles can be expressed in terms of their mesh (scale) and extremely fine particles in nanometers or micrometers (Barbosa-Cánovas et al., 2005c; Dhanalakshmi et al., 2011).

According to Nienow et al (1997), a feature that exists only for solid mixing is the ability to ‘unmix’ or in other words segregate. Segregation is often caused due to differences in particle size and density. Table 2.1 shows how the particle size is related to segregation risks.

Table 2.1-Influence of particle size on segregation tendency (data taken from Nienow et al., 1997)

Segregate Readily	Reduce Segregation	No appreciable Segregation
>75µm	<75µm	<10µm

It is seen that if the particle size is greater than 75 μm it can segregate readily which means that it can flow easily. When particle size decreases the inter particulate bonding forces such as the van der Waals, electrostatic and moisture bond forces increases and this can cause agglomeration that leads to flow and storage problems (Landillon, 2008; Nienow et al., 1997).

Particle size also influences the color and cohesion of a powder. When green tea leaves were super ground to fines the yellowness and the brightness increased (Hu, 2012). Powders can be categorised into free flowing and cohesive depending on their inter-particle forces and tendency to segregate. Free-flowing powders tend to separate more due to their ability to move independently. Cohesive powders on the other hand are obtained on mixing of interactive particles to give rise to an ordered mixture (Fan et al., 1990; Harnby, 1997c). When a fine particle is mixed with a large particle, it sticks to the larger particle due its cohesive forces (Williams, 1968). This helps to bind the particles together and prevents them from segregating. It is advised to use cohesive powders if the main objective is to obtain homogeneity in bulk mixing of powders. Sometimes in pharmaceutical and pigment dispersion applications cohesive particles are used in their mixing process to produce high quality mixtures by preferential bonding of particles (Harnby, 1997c). As the particles are not so free to move in cohesive systems it is tough to break the bonding and this gives a high level of mixture quality (Barbosa-Cánovas et al, 2005e; Harnby, 1997c).

As the particle size decreases, the contact area increases and the inter-molecular forces between the powders also increases thereby increasing the cohesion between the particles. It has been reported by Landillon et al (2008) that the cohesive properties of wheat flours was affected by the particle surface characteristics. Presence of fat, smooth surfaces and rough surface characteristics are some of the factors that contributed to the cohesive differences between the soft and hard wheat flours particles. In case of cream soup concentrates used in a study by Janjatovic et al (2011), it was seen that as the particle diameter decreased the cohesion between the particles increased due to more particle-particle interactions (Janjatovic et al, 2011).

Rumpf's (1962) work gives a good indication of the flow characteristics of a mixture and the magnitude of forces acting on them. Consider that at a tensile strength of

0.01kg/cm² a cohesive powder turns into free flowing, and then the critical particle sizes for each of the bonding mechanisms can be identified. Van der Waal's force act at a sub-micron level such as at a particle size less than 1 μm (Dhanalakshmi et al., 2011), the adsorption moisture force acts below 80μ, the capillary forces act below 500μ and sintered forces act on bigger particles (Harnby, 1997c). Adsorbed moisture increases the van der Waal's forces of attraction since the inter particle distance reduces as the adsorbed layers can be considered as parts of particle itself (Coelho, 1978). Rumpf (1962) also suggested that for particles with less than 1μm in size van der Waal's forces will be dominant and for coarser ones it would be adsorbed layer bonding. Figure 2.10 explains this in a better way.

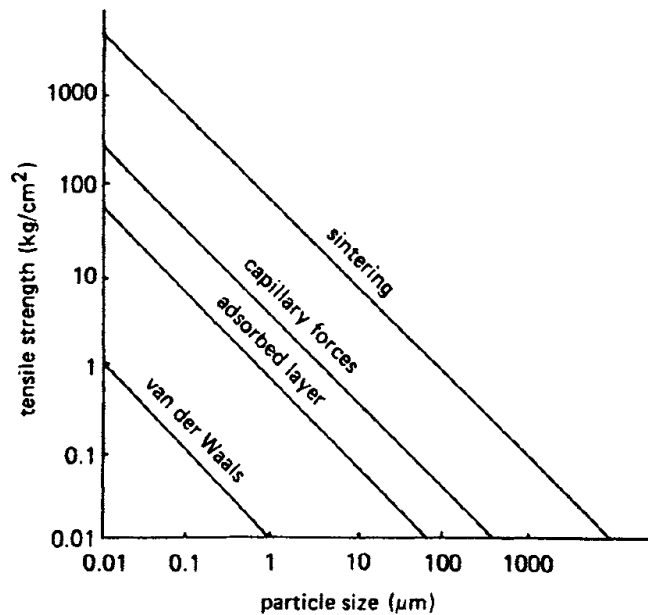


Figure 5.6 Theoretical tensile strength of agglomerates (Rumpf¹²)

Figure 2.10- Forces that act at different particle sizes (Harnby, 1997c) (original picture from Rumpf, 1958)

It is not easy to quantify the size of a particle if it has an irregular shape. Some ways of describing irregular particles is by using equivalent spherical diameter, equivalent circle diameter or statistical diameter (Barbosa-Cánovas et al., 2005c). Different methods can be used to classify the particle sizes (granulometry) such as sieve analysis, image analysis and laser analysis. In sieve analysis the particles are usually separated in a sieve shaker with mesh of different sizes and this gives good results for powders with size more than 50μm whereas laser analysis techniques are more suitable to classify

finer powders. A Malvern mastersizer is an apparatus that works on Fraunhofer Diffraction principle where the particles scatter the laser light beam to different intensities based on their particle sizes. (Mikli et al, 2000; UCC). Table 2.2 shows the size of some food products.

Table 2.2- Median particle size of some common food products (Barbosa-Cánovas et al., 2005c)

Commodity	B.S. mesh	Microns
Rice and barley grains	6–8	2,800–2,000
Granulated sugar	30–34	500–355
Table salt	52–72	300–210
Cocoa	200–300	75–53
Icing sugar	350	45

Particles can have many shapes such as dendritic, angular, fibrous, flaky, granular, irregular, modular and spherical (Dhanalakshmi et al., 2011; Mikli et al, 2000). Variations of shapes in food powders are large and range from highly irregular shapes to approximate spherical shape. Shape variations in particles being mixed can influence the mixture quality of the powders. It was reported that if a mixture contains mostly coarse particles and majority of them possess a plate like or fibrous shapes then the chances of segregation can be reduced, (Nienow et al., 1997). Generally, spherical shapes are preferable to obtain good flowability of powders however, it is not that easy to make powders which are spherical as the mineral powders produced in industry usually have a polyhedron shape and only after attrition due to handling or grinding they get a spherical shape. Particles such as spices can be highly irregular in shape whereas those such as yeast can be spherical or granulated sugar can have a crystal like structure. The particulate food materials being organic in nature have larger differences in their individual grain sizes and shapes due to their complex chemical compositions (Barbosa-Cánovas et al., 2005c). For food powders as mentioned above they have a huge range of shapes even within the same particulate food material (Barbosa-Cánovas et al., 2005c; Mikli et al, 2000). Different instruments are available in

the market that can measure the powder shape based on microscopic techniques. Table 2.3 shows different shape names and their descriptions.

Table 2.3- General definitions for a particle shape (Barbosa-Cánovas et al., 2005c)

Shape name	Shape description
Acicular	Needle shape
Angular	Roughly polyhedral shape
Crystalline	Freely developed geometric shape in a fluid medium
Dendritic	Branched crystalline shape
Fibrous	Regularly or irregular thread-like
Flaky	Plate-like
Granular	Approximately equidimensional irregular shape
Irregular	Lacking any symmetry
Modular	Rounded irregular shape
Spherical	Global shape

2.7.2 Powder and particle densities

Particle Density

As discussed in section 2.7.1 the particle density and size are two key factors that affect the mixture quality of a product since they are the main causes for segregation. Larger the differences in particle density more the chances of segregation in powder mixtures. Lighter particles float atop and more fine and dense particles fall to the bottom on vibration as is commonly observed in a box of cereal mixture. Only two works suggested that particle density along with particle diameter ratio could be equally important in causing segregation tendencies in powders (Bridgwater, 1976; Drahun and Bridgwater, 1983). Most of the other studies mention density as an important factor but always give it minor importance as compared to particle size distribution while studying mixing behaviour and mixture quality of powders (Barbosa-Cánovas et al., 2005c; Nienow et al., 1997; Williams, 1976).

The total mass of particles divided by total volume of particles gives the particle density. Since particles can have open or closed pores and voids between them there are many definitions or ways, in which the density of a particle can be expressed. Some definitions that exist are true density, apparent particle density and effective density. True density is the actual density of the total solid content in the particle and does not take into account the pores present in its matter whereas in case of the effective density both the

open and closed pores are considered. The density of organic and food powders is generally less than that of mineral and metallic powders. Food powders have particle densities around 1000-1600kg/m³ (Barbosa-Cánovas et al., 2005c) . A gas pycnometer can be used to measure the apparent density. Here the nitrogen gas is used as a displacement medium to measure the displaced volume accurately. If the gas does not penetrate into the particles, then the displaced volume of the particles is measured, from which the particle density can be determined.

Bulk density

The bulk density and porosity are two important parameters which directly determine if powders can be mixed and also quality of a final powder mixture and are relevant when it comes to proper storage, setting product specification and also determination of flowability of the product (Barbosa-Cánovas et al., 2005a). Bulk density is an important property for the food companies to control the quality, storage, processing, packaging and handling conditions of a powder. The bulk density of a particle can be defined as “mass of particles that occupy a unit volume of the bed” and porosity can be defined as “the volume of voids within the bed divided by the total volume of the bed”. During storage of powders in bins, there are voids between the powder particles and on compression these voids get reduced and thus the bulk density increases. Food manufacturers need to consider this parameter specially when claiming the net weight in the label of the food (Barbosa-Cánovas et al., 2005a; Ganesan, 2008). Table 2.4 shows poured bulk density of some commonly used food powders.

There are three types of bulk density: aerated, tapped and poured (Barbosa-Cánovas et al., 2005a). The bulk and tapped density is usually measured by a simple tapping machine in which a certain volume of powder is filled inside the measuring cylinder and tapped for a fixed number of times. The new volume is measured after tapping stops automatically and by using the appropriate formula the densities are calculated. Tapped density is the density of a powder after it has been vibrated a certain number of times by tapping it.

Table 2.4-Poured Bulk density and moisture contents of different food powders (Barbosa-Cánovas et al, 2005a)

Powder	Bulk density (kg/m ³)	Moisture content (%)
Baby formula	400	2.5
Cocoa	480	3–5
Coffee (ground and roasted)	330	7
Coffee (instant)	470	2.5
Coffee creamer	660	3
Corn meal	560	12
Corn starch	340	12
Egg (whole)	680	2–4
Gelatin (ground)	680	12
Microcrystalline cellulose	610	6
Milk	430	2–4
Oatmeal	510	8
Onion (powdered)	960	1–4
Salt (granulated)	950	0.2
Salt (powdered)	280	0.2
Soy protein (precipitated)	800	2–3
Sugar (granulated)	480	0.5
Sugar (powdered)	480	0.5
Wheat flour	800	12
Wheat (whole)	560	12
Whey	520	4.5
Yeast (active dry baker's)	820	8
Yeast (active dry wine)		8

2.7.3 Flow properties

Flowability is the ease with which a powder can flow out of the bin (Barbosa-Cánovas et al, 2005a). Flowability affects the mixing ability of powders, how the powder can be handled, stored, packaged and transported. It is generally difficult to predict the flow characteristics of food powder mixes because they contain different types of ingredients and also experience varied storage conditions (Fitzpatrick et al., 2010).

Flow problems and segregation problems (demixing problems) are correlated such that if a powder experiences flow problems it is less likely to experience segregation and vice versa (Nienow et al., 1997). Since segregation is the reverse of mixing it can be thus inferred that if flow problems exist mixing can take place and vice versa. However this cannot be the case for all powders since usually powders with flow problems are cohesive in nature and it is not necessary that they tend to mix well due to increased adhesion. This depends on other factors as well such as the energy applied for mixing

and also how strong the agglomeration is if any or the bonds are between the powders and how tough it is to break them. On the other hand if powders are extremely free flowing in nature some amount of moisture could help them to mix better thereby reducing the segregation tendencies (Nienow et al., 1997). This will be discussed in the subsequent sections. In other words, powders that are very cohesive are less likely to segregate but may experience greater flow problems and powders which are free flowing in nature can flow easily but may experience segregation.

In any mixed product the flow of the final powder is very important to ensure that the product can be discharged into the specific containers in a consistent manner. The study of rheology plays an important role in the food industry for applications such as food acceptability, processing and handling (Tabilo-Munizaga and Barbosa-Cánovas, 2005). Since powder flow can be considered as a bulk movement of the powder particles it is important to understand the bulk properties and how they can affect the system (Barbosa-Cánovas et al., 2005c). When bulk properties are considered the powder system is viewed as a whole unit and its properties are classified. Bulk properties include size, geometry and surface characteristics of individual particles and properties such as bulk density and porosity are useful to predict if the particle can be well packed in a container (Barbosa-Cánovas et al., 2005a).

Particle size is one of the main factors which influence the flowability of the powders. Particles with size above 200 μm are easy flowing in nature compared to the fine powders which experience greater cohesion and thus reduced flowability (Dhanalakshmi et al., 2011; Ganesan, 2008; Teunou et al., 1999). When the particle size of 26% fat milk powder was reduced from 239 μm to 59 μm it drastically influenced the flow behavior of the powder from being easy flowing to very cohesive in nature (Fitzpatrick et al., 2004). On reducing the size of the particles their flow turns cohesive since their surface area per unit mass increases which in turn increases the cohesive forces between them (Fitzpatrick et al., 2007). Studies by Tenou et al (1999) proved that a combination of the moisture content and particle size is a decisive factor for flowability. Skim milk powder that had low water content and large particle size was easy flowing whereas flour with higher water content was more cohesive and difficult to flow (Teunou et al., 1999). Presence of moisture content in the powders causes

stickiness and cohesive bonding in the powders leading to decreased flowability (Fitzpatrick et al., 2007).

Other factors such as storage & handling conditions and fat content of powders can also affect flowability (Fitzpatrick et al., 2007; Ganesan, 2008). However when Fitzpatrick et al (2004) studied seven 26% fat milk powders with similar physical properties and varying free fat content in the range of 12.6 to 74.2%, they observed that free fat content had little influence on cohesion and flowability.

Some studies have (Dhanalakshmi et al., 2011; Mikli et al, 2000) mentioned that the properties such as bulk density, flowability and compressibility depend on particle shape and size which the author considered to be the main characteristics of powders that in turn affect flowability of powders. Cohesion, adhesion (particle wall attraction), friction and gravity are other major parameter that affects flowability of powders (Barbosa-Cánovas et al., 2005a; Dhanalakshmi et al., 2011). Cohesion (inter-particle attraction) between fine particles tends to make the powders sticky or agglomerated and thereby hinder its flow out of the container (Barbosa-Cánovas et al., 2005a; Harnby, 1997c). For a powder to flow easily out of the bin the strength of the powder has to be less than the forces acting on it and therefore it has to fail.

2.7.4 Empirical Measures of Flowability

Angle of Repose

It has been used as a rough indicator to measure flowability. It is not relevant for powders that are cohesive in nature but they can be used to estimate the flowability of non-cohesive powders by pouring the powders on a flat circular surface through an orifice and measuring the drained and poured angle of repose (Barbosa-Cánovas et al., 2005a). Table 2.5 shows the angle of repose for different degrees of flowability of the powders (Carr, 1976).

Hausner Ratio

Hausner ratio is the ratio of tapped bulk density to loose bulk density and it gives a rough indication of the powder flowability. It can also be used to quantify the compressibility of the powders (Ganesan, 2008). A Hausner ratio of less than 1.25 indicates an easy flowing powder whereas more than 1.4 indicates a powder with flow

problems. Hausner Ratio is sensitive to the powder shape (Barbosa-Cánovas et al., 2005a).

Table 2.5-Flowability determination from angle of repose (Carr, 1976)

Angle of Repose	Flowability
35°	Free flowability
35° -45°	No free flowability
45° -55°	Very high cohesiveness
>55°	No flowability

2.7.5 Composition and moisture content

Composition

The amount of certain type of powder if present in more quantities than the others can also influence the mixture quality and mixing time. On mixing dry hard and soft wheat flours in the same ratio it took longer time to mix than when a higher amount of hard wheat flour was present (Kuakpetoon et al., 2001). In this case this could have been caused due to the differences in particle size for both the flours. On mixing ballotini / ballotini powders with same size ratio but for two different compositions the mixture quality was similar but the standard deviation (concentration of coarse particle) was higher when equal quantities of the two differently sized ballotini was used as compared to the one which had lesser amount of coarse particles (Coelho and Harnby, 1979). Thus it can be concluded that ratio of powders used does affect the mixing behaviour of powders when same size ratio is used.

Moisture Content

Moisture content can improve or deteriorate the mixture quality of food powders. Trials were conducted by Harnby (1997) using ballotini/ballotini and sand/sand particles with a size ratio of 2:1 in a V-mixer. For ballotini mixture as seen in Figure 2.11, under dry conditions and at low moisture contents the mixture quality is very good but as

moisture increases, for that small range the quality reduces and then improves again at higher moisture contents. The initial state is due to the electrostatic charging between particles and the reason for the intermediate deterioration is attributed to the free flowing nature of particles due to lack of sufficient contact area that makes the powders segregate from each other. However, as the moisture content further rises such that critical humidity is gained the cohesiveness between particles increases causing the formation strong liquid bridges between the particles and this helps to give a good mixture quality (Harnby, 1997c). In the sand mixtures (Figure 2.11) the increase in moisture content does not cause much improvement in mixture quality. It has surface charge dissipation because of the angular nature of particles. Due to increased contact area compared to Ballotini, the adsorbed layer bonding is more and presence of liquid bridges improves the mixture quality in two stages mixing (Harnby, 1997c). Similarly studies done in a highly segregating mixer such as a Y- cone mixer shows that small additions of moisture can drastically improve mixture quality for both spherical and granular particles mixture (Coelho and Harnby, 1979).

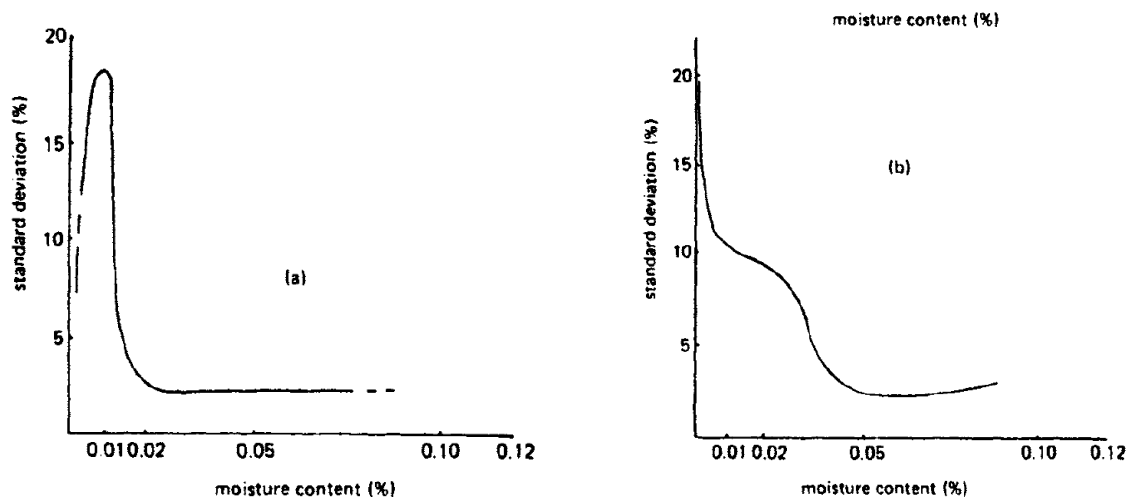


Figure 2.11- The effect of moisture content on the mixing quality for (a) Ballotini and (b) Sand mixture (Harnby, 1997c)

The amount of moisture present in a powder highly determines its shelf life, its microbial quality and also its other physical properties (Ganesan, 2008; Goula and Adamopoulos, 2008; Palzer, 2005). Presence of moisture is one of the key causes for caking of powders (Fitzpatrick et al., 2010). Increase in moisture content causes an increase in cohesion of the powders and reduces their flowability (Fitzpatrick et al., 2007; Ganesan, 2008; Landillon, 2008; Teunou et al., 1999). During spray drying of tomato powders in order to prevent stickiness and also to control powder properties such as hygroscopicity and bulk density, the moisture content was controlled by adjusting the temperature of the exhaust air that circulates inside the chamber (Goula and Adamopoulos, 2008). When powders are exposed to different relative humidity they can adsorb or desorb moisture. The relationship between the moisture content and water activity for the powder when placed in such different atmospheres is depicted by the moisture sorption isotherm or the water sorption isotherm (Carter and Schmidt, 2012; UCC). It is a plot between the water content at equilibrium X_e and the relative humidity RH. These isotherms are a useful tool to predict the caking behavior of food powders and also to predict the critical relative humidity for a given substance at a given temperature. By using water sorption isotherms it is easier to understand why certain powders take longer time to mix and can be used to find the optimum moisture content that can enable faster mixing and also to evaluate the best storage conditions for powder mixtures that contain ingredients that can easily agglomerate. Numerous studies have used the water sorption isotherms to predict the behavior of powders under varied moisture conditions, temperature and also to estimate their other properties such as glass transition temperature or caking behavior (Mathlouthi and Rogé, 2003; Silalai and Roos, 2010). Water content can also influence the color of products which is an important attribute in many foods (Ladrón de Guevara et al., 2002; Rhim, 2011; Topuz, 2008).

2.7.6 Glass Transition Properties

Glass transition temperature (T_g) is defined as the temperature at which the amorphous glass-like substance changes from glassy state to a more viscous rubbery state.

Operating at temperatures below T_g can make a powder sticky and very cohesive and this can influence mixing and segregation. Below T_g the substance is in a solid form (glassy state) and above this temperature they become soft and rubbery due to the

associated viscosity changes (Fitzpatrick et al, 2006; Jaya and Das, 2009; Palzer, 2005). Moisture content or addition of water acts as the plasticizer and decreases the T_g thereby influencing the mixture quality of the powders by changing their surface properties such as cohesion (Carter and Schmidt, 2012; Fitzpatrick et al, 2006; Palzer, 2005; Thomas et al., 2004). The Gordon-Taylor equation given below can be used to estimate the T_g of the binary mix of a glass forming compound S that is miscible in water.

$$T_g = \frac{w_w T_{g,w} + k w_s T_{g,s}}{w_w + k w_s} \quad (3)$$

In the above equation, T_{gs} and T_{gw} are the glass transition temperatures of the substance S and water and w_s and w_w are the mass ratio of S and water. K is a fitting parameter (Fitzpatrick et al, 2006). Gordon-Taylor equation was used to predict the T_g of fruit powders at different moisture contents in the work by Jaya and Das (2009). Glass transition temperature also affects the stickiness characteristics of food powders. Many studies have reported that in case of milk powders, the amorphous lactose dominates the glass transition temperature and therefore causes stickiness in their powders (Fitzpatrick et al, 2006; Lloyd and Chen, 1996; Silalai and Roos, 2010). Some applications of glass transition temperature related mechanisms are staling of bread and crunchiness of snacks (Berk, 2009). Glass transition temperature can be used as an indicator of food stability and also to predict caking and stickiness mechanisms in food stuff (Abbas et al., 2010).

The commonly used method to evaluate the T_g is by the use of Differential Scanning Calorimetry (DSC) (Berk, 2009; Fitzpatrick et al, 2006). This machine measures and records the heat capacity of the sample and the reference as a function of temperature. A steep decrease or increase in the heat capacity measurement will indicate an exothermic or endothermic reaction at that temperature. The specific heat C_p of a substance can be defined as the amount of heat (kJ) required to increase the

temperature of one unit mass (kg) of the material by 1 degree Kelvin at constant pressure (Berk, 2009). It is one of the most basic thermal properties.

In Figure 2.12 the water activity, moisture content, glass transition and sticky point temperature have been plotted for pineapple powder and it is seen that as the water activity increases the T_g and sticky point temperature (T_s) decreases (Jaya and Das, 2009).

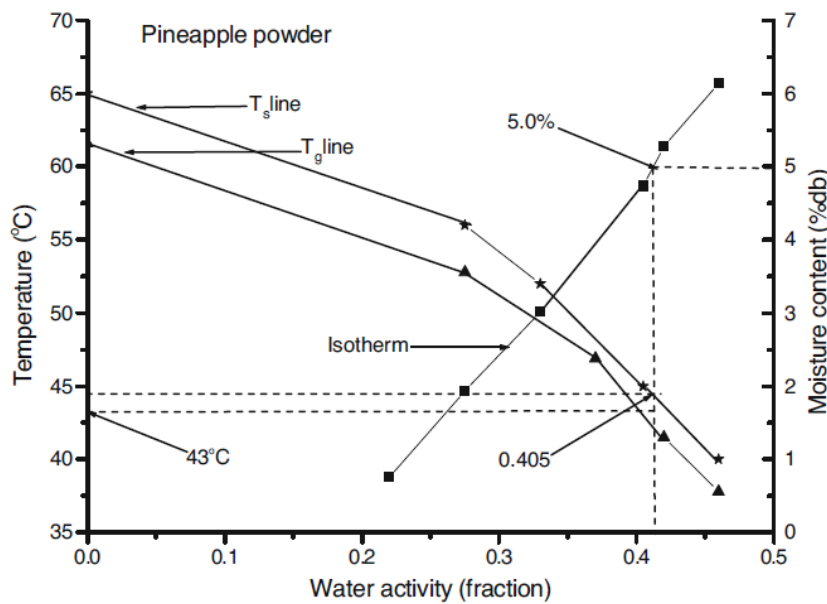


Figure 2.12- Glass transition and sticky temperatures vs water activity for pineapple powder (Jaya and Das, 2009)

In this study it was attempted to measure T_g of the spice powders to find the temperature above which they tend to become sticky and cohesive as this can influence the mixing, however it was not easy to obtain a T_g for the range studied and further attempts were not made to study T_g for these materials.

2.7.7 Agglomeration and Caking

Caking is a serious issue for the food industry as it can reduce the value of a product by making it undesirable for customers. If the powders have a tendency to cake due to

presence of moisture this can influence the ability to mix well with other powders and can result in an agglomerated product instead of a good mixture. In some cases the strength of the caked powder can be so high that it can be impossible to use these powders for mixing. For amorphous compounds caking takes longer time and happens in the presence of moderate moisture and pressure conditions. Humidity, consolidation and temperature all together can cause powders to cake (Freeman, 2011). Most of the food powders such as meat, fish, dairy, vegetable and fruit powders have amorphous solids and in the presence of increasing temperature the mobility between the molecules increases thereby making them more viscous and rubbery and in turn more sticky and cohesive in nature. This was shown in a study by Fitzpatrick et al (2006) where caking of milk powders took place after exposing commercial skim milk powders to 76% relative humidity for specific time intervals; the glass transition temperature disappeared which led to the mobilization of lactose and made the powders sticky. Several adhesion mechanisms can take place amongst the particles depending on the strength of their inter-particle attraction and the pressure. As shown in Figure 2.13 liquid bridges can be formed due to the effect of the capillary forces; viscous bridges can appear due to viscous flow and the contact area can increase due to the increased viscoelastic deformation. When particles form a bridge amidst them due to the pressure or surface tension induced viscous flow, the process is known as sintering (Palzer, 2005). All these mechanisms contribute towards powder agglomeration and in turn caking of powders, which can influence the ability to mix powders with ease.

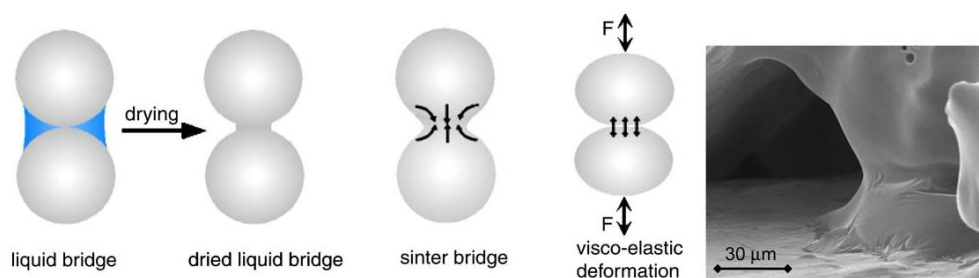


Figure 2.13- Important adhesion mechanisms leading to food agglomeration and an example of a viscous sinter bridge (Palzer, 2005)

CHAPTER 3

METHODOLOGY

In this chapter, the materials and methods that were used for major part of the work have been described. However, additional details and specific methods that pertain to a particular chapter are described in that chapter, such as water activity measurement in chapter 5.

3.1 Physical property measurements

3.1.1 Particle size

The particle size of all the powders used in this study was measured using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) except for the larger sized particles, i.e. oregano and salt Medel (Santa Maria AB, Sweden). These two powders were measured using sieve analysis since their particles were too big to be measured in the Malvern Mastersizer 2000. Sieve analysis was performed by using the FRITSCH Vibratory Sieve shaker Analysette 3 PRO (Fritsch GmbH, Germany). The particle size distribution of all the powders measured is presented in inTable 3.1. The average value from six replicates has been given below.

Table 3.1-Particle size distribution of all the powders (sorted by median particle size)

Name of Powder	Particle Size Distribution (μm)		
	d (0.1)	d (0.5)	d (0.9)
Salt Medel (Salt M)	1250	1460	1600
Salt Siede (Salt S)	538	993	1572
Salt Vaccum (Salt V)	367	692	1185
Salt Extrafine (Salt EF)	32	110	253
Salt	231	436	718
Oregano	1250	1600	-
Thyme	437	863	1488
Sugar 500	236	542	1022
Onion Granules	185	364	626
Black Pepper	72	345	706
Paprika	67	223	485
Sugar 315	82	212	372
Cumin	55	207	503
Dextrose	51	187	441
Yeast	10	63	160
Potato Starch	24	44	75
Onion powder	5	40	167

3.1.2 Particle density

To measure the particle density a Micromeritics AccuPyc II 1340 gas pycnometer (Micromeritics Instrument Corporation, USA) was used which used Nitrogen gas for the volume measurement. The density data for all the powders is listed in Table 3.2. The data is the average value taken from six replicates.

3.1.3 Bulk density

The poured and tapped bulk density of the powders was measured using a J. Engelsmann Jolting Volumeter type STAV II (J. Engelsmann AG, Germany). A constant mass of powder was poured into the cylinder tube and the volume was measured to

determine the poured bulk density. Subsequently, the cylinder was tapped 1250 times and the powder volume was measured again, from which the tapped bulk density was determined. The poured, bulk and particle densities for each of the powders are provided in Table 3.2.

Table 3.2- Density data for all the powders (sorted by poured bulk density)

Name of powder	Poured Bulk Density (kg/L)	Tapped Bulk Density (kg/L)	Particle Density (kg/L)
Salt	1.283	1.403	2.165
Salt Extrafine (Salt EF)	1.267	1.434	2.158
Salt Vacuum (Salt V)	1.182	1.262	2.155
Salt Medel (Salt M)	1.085	1.151	2.132
Salt Siede (Salt S)	1.061	1.141	2.134
Sugar 315	0.860	0.969	1.586
Sugar 500	0.857	0.947	1.589
Potato Starch	0.699	0.783	1.447
Dextrose	0.688	0.828	1.524
Onion Granules	0.649	0.702	1.510
Onion powder	0.548	0.788	1.522
Paprika	0.454	0.517	1.364
Yeast	0.441	0.534	1.153
Cumin	0.386	0.484	1.315
Black Pepper	0.371	0.438	1.343
Thyme	0.176	0.212	1.270
Oregano	0.066	0.073	1.208

3.2 Mixing in paddle mixer and Sampling

A 2 L prototype paddle mixer made of Plexiglass (made by TetraPak, Lund) and a thief probe sampler with dimensions 300mm length, 19mm diameter and 10ml tip (from Sampling Systems Ltd., UK) was custom built for this project (Figure 3.1a and c).

Powders were placed side by side in the paddle mixer to represent a fully segregated medium and the worst-case scenario (Aissa et al., 2011) of mixing. The mixer speed was determined based on the Froude number. The Froude number (Fr) is a ratio between the centrifugal and gravitational forces and the formula used to calculate the number is shown in equation 1. At lower Froude number such as 0.18, the mixing progressed slowly, and at higher Froude numbers close to 1, the bed was overly fluidised. Consequently, a Froude number of 0.65 was chosen and the corresponding mixer speed was 35Hz.

$$Fr = \frac{v}{\sqrt{gL_c}} \quad (1)$$

where

v , tip speed (m/s) = 0.47 m/s

L_c , paddle length (m) = 0.053 m

Mixing times of 10, 15, 30, 90 and 150 s were chosen for sampling in each trial since it was seen that most of the mixing took place in the first 30 seconds and it was continued until 150 s to check if mixing was followed by any demixing. In the process industries, usually good mixture quality is obtained within 90 seconds of mixing (personal communication). Nine fixed sampling points were chosen across the mixing zone (Figure 3.1b) and the samples were withdrawn at each interval during mixing using a thief probe sampler or a bent spoon as shown in Figure 3.1c and d. For some experiments that will be discussed in further chapters due to the shapes, sizes or water content of the powders it was easier to withdraw samples using a bent spoon instead of the thief probe sampler since the constricted opening of the thief probe could get blocked when used to sample cohesive powders from the mixer bed. In industries, it is common to use a thief probe sampler or a slot sampler based on the type of powder mixture which needs to be sampled. In case of free flowing powders, usually a powder

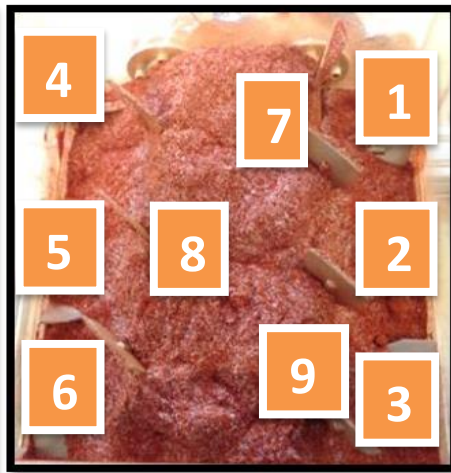
thief is used and in case of cohesive mixtures a slot sampler is used. In this study as the size of the mixer was very small compared to that of an industrial mixer, it was not possible to use a slot sampler as it could get stuck with the mixer blades and hence only powder thief or bent spoon was employed. Although thief probe sampling method disturbs the mixer bed and the original state of mixing of the powders and has been reported to give biased information due to analytical and sampling errors (Muzzio et al., 1997), it is still the most commonly used method across industries and is has the following advantages:

- 1) It is easy to use for sampling
- 2) Provides good reproducibility and repeatability of results
- 3) Able to provide representative samples from the bulk

(a) Paddle Mixer



(b) Sample zones



(c)



(d)



Figure 3.1- (a) 2L paddle mixer (b) mixer showing the nine sampling points. (c) thief probe sampler (d) bent spoon

3.3 Assessment of mixture quality using a salt conductivity method

The samples taken from the mixing trials were diluted using deionised water to a specific concentration which depended on the powders being mixed. For example, in the case of paprika / salt (P/S) mix 2g of the sample was used and diluted to 50g/l using deionised water and in the case of oregano / salt (O/S) mix 0.2g sample was used and diluted to 10g/l using deionised water. The diluted samples were placed inside a shaking bath that was operated at 180 rpm for 1h to ensure that all salt is dissolved. The conductivity of the samples was measured using a SevenGo SG78 conductivity probe, Mettler Toledo. A standard salt calibration curve was prepared by measuring the conductivity of salt at different known salt concentrations. The conductivity of individual spices such as paprika and oregano and the binary mixtures P/S and O/S was also measured and the curve was prepared but it was seen that the interference from these powders was very less and could be ignored. Hence, only the salt calibration curve was used for the calculations (Figure 3.2).

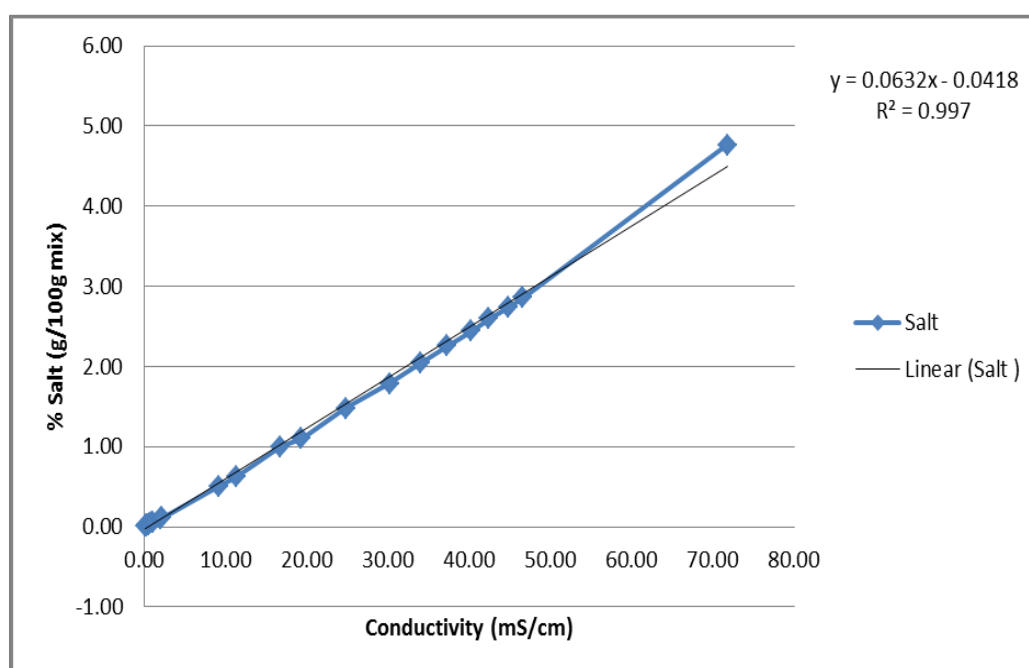


Figure 3.2- Standard salt calibration curve

From the conductivity measurements of the samples, the salt concentration in each of the samples was evaluated by using the slope equation from the calibration curve. The sample variance (S^2) was then evaluated by inserting these data into equation 2.

$$S^2 = \frac{\sum_{i=1}^9 (C_i - C_{average})^2}{9} \quad (2)$$

where:

C_i salt concentration in sample i

$C_{average}$ average concentration of salt

The mixture quality of a binary mixture was assessed by evaluation of the coefficient of variation (CoV) in equation 3.

$$CoV = \frac{S}{\mu} \quad (3)$$

where:

S sample standard deviation

μ target composition of salt

CoV is more useful than S^2 or S in providing an insight into how the target component concentration influences mixture quality. The standard deviation depends on the sample size and also does not account for the concentration differences and hence can give misguided results (Williams, 1968). As the target component concentration becomes smaller, sample standard deviation tends to decrease due to the smaller values of concentration, and this can hide the reality that mixture quality tends to get worse with decreasing target component concentration (Weinekötter, 2007). Consequently, CoV is better for comparing mixture quality when trying to evaluate the influence of target component concentration on mixture quality.

In food and pharmaceutical industries in order to release new products into the market and to ensure that the products manufactured have consistent performance and quality they use certain indices to assess the quality of the product. One such index to ensure

satisfactory mixture quality is the CoV, which should be below 0.06 or 6% (Berthiaux et al., 2008; Marikh et al., 2008).

3.4 Determination of Mixing Powder Mass and Sample size

The mass of powders used for mixing varied depending on the type of powders used and the composition of the powder mix. For example, for P/S mixture a 2 kg mass of powder was used for a 50% salt mixture, while 300 g was used for O/S mixture with 50% salt. In order to cover the blades of the mixer and get sufficient powder for mixing, the total mass for each type of binary mix had to be specifically chosen so as to enable mixing for different compositions.

The sample size used for the salt conductivity measurements also differed for each type of powder mix depending on the nature of powder used. For example, for the P/S mix sample size was 2 g whereas for O/S mix the sample size was 0.2g because of the much lower mass of O/S in the mixer and to facilitate ease of sampling. Since the sample size between the two binary mixes P/S and O/S was different from each other and sample size can influence the CoV values, trials were conducted to investigate the effect of sample size for P/S and O/S. The CoV for 50% P/S with 2 g sample size and 50% O/S with 0.2 g sample size was 0.06 and 0.25 respectively at the end of mixing and on decreasing the sample size of P/S mix to 0.2g which is the same as that of O/S sample size the CoV increased to 0.11 but this was still better than the CoV attained for O/S mix at the end of mixing (Figure 3.3). It was not possible to increase the sample size of oregano to 2 g since withdrawing 2g of powders for each sample would highly reduce the available quantity of powders for mixing. Also the sampling of O/S was not as easy as it was for other powders since the leaves have a tendency to disperse and due to the segregating nature of the mixture the transferring process of the O/S mixture for conductivity analysis could be biased in terms of particles chosen for analysis though the best attempt was made to use a mixed sample.

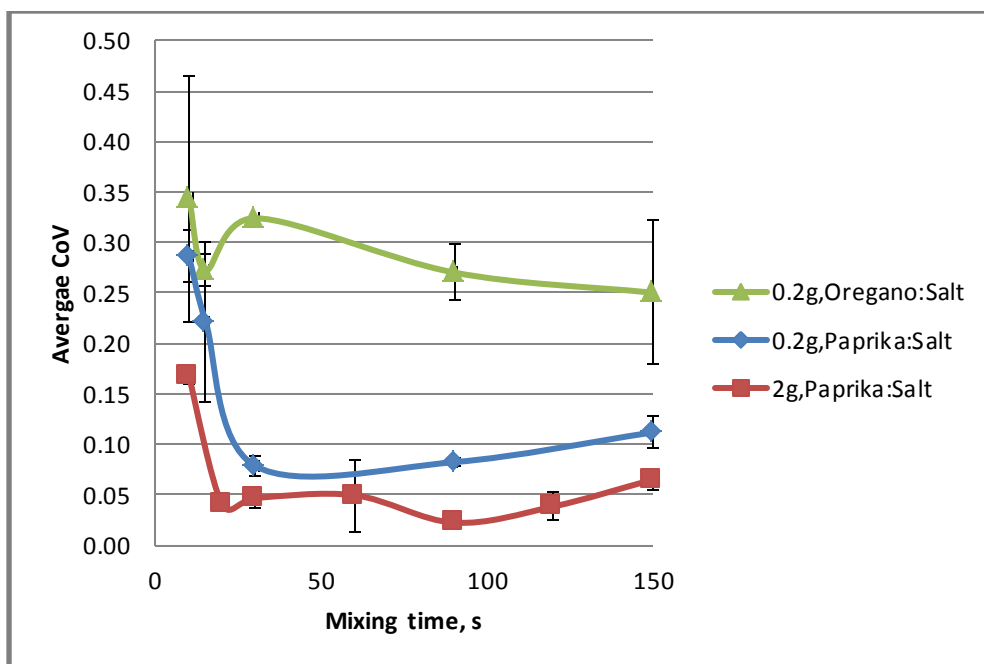


Figure 3.3- Effect of sample size for P/S and O/S mixtures

CHAPTER 4

APPLICATION OF DIGITAL COLOUR IMAGING METHOD TO ASSESS THE MIXTURE QUALITY OF BINARY FOOD POWDER MIXTURES

Digital colour imaging (DCI) was applied in this study as a novel approach for assessing the mixture quality of binary food powder mixes. Three different binary powder mixes with different coloured ingredients [salt, paprika, black pepper and onion] were investigated using a commercially available system called DigiEye. The coordinates of CIELAB colour space were used to describe the colour of the samples. The sample colour variance was used as a measure of mixture quality. The results showed that DCI has potential for assessing the mixture quality of binary food powder mixes, provided that colour difference between the powders can be measured. The ability to assess mixture quality decreases as the colour difference between the components in the mix decreases. Furthermore, scale of scrutiny and composition also influence the capability of this method.

Nomenclature

DCI	Digital Colour Imaging
L^*, a^*, b^*	CIELAB colour coordinates (Range L^* +33.7 to +96.7, a^* -0.2 to +35.2, b^* +0.8 to +39.0)
$L^*_{\text{standard}}, a^*_{\text{standard}}, b^*_{\text{standard}}$	CIELAB colour coordinates for white space
ΔE	colour parameter relative to white space
N	Number of squares in the image
μ	Average ΔE for well mixed sample
Variance ΔE	Variance in ΔE values for N squares
Variance ΔE_{NM}	Variance in ΔE for non-mixed powders

4.1 Introduction

Powder mixing is a complex operation that requires knowledge of powder properties such as powder size, shape, bulk density, particle density, mixer design and mixing conditions. Mixing operations are undertaken to manufacture multi-component mixtures with the best homogeneity and consistent product performance (Aissa et al., 2011). A homogeneous mixture is one in which the composition of all constituents are uniform throughout the whole mixture and one of the important steps post mixing is to be able to assess the state of homogeneity of the mixture (Aissa et al., 2010b; Fan et al., 1970). In many food industries, there is little or no objective assessment of food powder mixture quality and there is a need in industry for quick and user-friendly techniques that are potentially faster for analyzing mixture homogeneity, such as near infra-red spectroscopy (Kehlenbeck, 2011) and image analysis (Aissa et al., 2011). Image analysis techniques are becoming increasingly popular due to the speed of analysis, lower costs and also because they are simpler to use (Aissa et al., 2010b). They can be used as a complementary method with the traditional methods e.g. along with particle sizing methods where it acts as a means to validate the data obtained (Boschetto and Giordano, 2012). Traditional methods to evaluate the powder mixture homogeneity include use of thief probes for sampling followed by estimation of particle size

distribution (Boschetto and Giordano, 2012) or measurement of conductivity when salt is one of the ingredients or application of UV spectroscopy when active ingredients are used (Muzzio et al., 2003). Thief probe sampling leads to destruction of the original state of the powder bed as compared to image analysis techniques that are non-destructive and faster to use in on-line systems (Berthiaux, 2006; Muzzio et al., 2003). However one drawback with image analysis is that lighting conditions may not be stable and thus require background correction on each image to avoid errors during analysis (Berthiaux, 2006; Le Coent, 2005; Muerza, 2002). In the spice industries where food powder mixtures are produced with many ingredients that vary in shape, size, colour and texture (Barbosa-Cánovas et al., 2005c), colour and the visual appearance is of prime importance to appeal to the customer. In industry, in order to determine the optimum mixing time for a particular mix and to assess the mixture quality, the manual assessment of mixture quality is sometimes undertaken by visual inspection of the uniformity of colour within the mix. In fresh produce industry, such as in harvesting and purchase of fruits and vegetables, visual assessment of colour plays an important role in determining the value of the product and to judge if it is ripe enough (Jha and Matsuoka, 2000; Ji et al., 2013). However, visual assessment in the food industry needs to be standardized since this can vary depending on the person assessing the sample, the illumination conditions and the angle of observance. Thus, there is a need to investigate the application of objective assessment methods, which are quick and reliable to assess the mixture quality in industry. Colour imaging can help to track every particle since the colour of each pixel has specific values in the Red Green Blue (RGB) coordinates (Aissa et al., 2010b). Previous studies that have applied colour assessment method have been to assess the ripeness of banana (Ji et al., 2013), the firmness of mangoes (Jha et al., 2006) and to correlate the surface gloss with weight of eggplant during its storage (Jha et al., 2002). Hunter L, a, and b values and maturity index were modeled to evaluate maturity of mango by non-destructive means (Jha et al., 2007). The objective of this study was to explore the application of digital colour imaging (DCI) for assessing food powder mixture quality and to highlight any problems and limitations associated with it. The DCI system used in the study was DigiEye, which has a high-resolution camera and a sample chamber with controlled lighting conditions for imaging the sample.

4.2 Materials and methods

4.2.1 Powders and binary mixes

The food powders used were paprika, salt, black pepper and onion. All the powders were obtained from Santa Maria AB, Sweden. The binary powders mixes used were:

Paprika – Salt

Black Pepper – Salt

Onion - Salt

Three composition recipes (by mass) were mixed for each of the binary mixes, which are 30: 70; 50: 50 and 70: 30. The volume mean diameter, $D[4, 3]$, for salt, paprika, black pepper and onion powders is 454 μm , 252 μm , 369 μm and 65 μm , respectively.

4.2.2 DigiEye and its operation

The digital colour imaging system (DigiEye), sourced from VeriVide Ltd UK is a complete non-contact colour imaging and measurement system. This equipment consists of a digital camera Nikon D90 with an image quality of 12.3 megapixels and a sample chamber with fluorescent D65 illuminant to provide controlled light conditions inside the cabinet. This helps the collection of same quality high resolution images which do not require background lighting correction. It has the ability to measure colour at many points of the sample region. The colour measurement data is reported as colorimetric values such as XYZ and CIELAB and spectral reflectance between the ranges of 400nm to 700nm with an interval of 10nm. The DigiEye has been used for colour assessment in both the food industry and textile industry (DigiEyeUserGuide - version2.43, 2007; VeriVideLtd., 2010).

4.2.3 Mixing procedure and assessment of mixture quality

The binary powder mixes were prepared by weighing the required amount of ingredients in a plastic transparent bag kept on a calibrated weighing scale. In each trial the total amount of binary mix prepared was 100g. The bag was tied and then shaken manually by rotating the bag right and left (to mimic a tumble mixer type of movement). The extent of mixing equalled the number of times the bag was shaken from right to left. Trials were undertaken whereby binary powder samples were shaken for a different

number of times in order to mimic a progression in mixing. In some trials, the powders were shaken many times, approximately 10 to 15 times, to obtain “well-mixed” powders or what were perceived to be well mixed to the human eye.

At the end of mixing the powder, mixture was poured onto a custom made transparent Plexiglas dish [100×100×10 mm] and levelled using a ruler. The sample was placed inside the DigiEye chamber and an image of the mixture in the dish was clicked using the DigiEye camera and the measurement was done with the help of its calibrated software. The image was virtually divided into 25 or 100 small squares, as illustrated in Figure 4.1. For each square the CIELAB colour coordinates L^* , a^* and b^* were measured and ΔE (the colour value relative to white space) was calculated from equation 1.

$$\Delta E = \sqrt{(L^* - L_{standard}^*)^2 + (a^* - a_{standard}^*)^2 + (b^* - b_{standard}^*)^2} \quad (1)$$

where $L_{standard}^*$, $a_{standard}^*$ and $b_{standard}^*$ are the values measured for white space.

The variance in ΔE (Variance ΔE) was used as a measure of mixture quality of the powder mix and this was calculated from equation 2.

$$Variance \Delta E = \frac{\sum_{i=1}^N (\Delta E_i - \mu)^2}{N} \quad (2)$$

where μ is the average ΔE for well-mixed sample and N is the number of squares in the DigiEye image.

The variance in ΔE for a non-mixed powder mix at the beginning of each trial (Variance ΔE_{NM}) was calculated from equation 3 and then applied thereafter.

$$Variance \Delta E_{NM} = N_P (\Delta E_P - \mu)^2 + N_S (\Delta E_S - \mu)^2 \quad (3)$$

where N_P and N_S are the mass fractions of the ingredient powder (paprika or black pepper or onion) and salt, respectively and ΔE_P and ΔE_S are the ΔE values for the ingredient powder and salt respectively (note: salt is used in all the binary mixes).



Figure 4.1- Digi Eye image of paprika powder partitioned into 25 squares

4.2.4 Repeatability studies

Triplicate trials were performed for all the well mixed samples and good repeatability was obtained with standard deviations in ΔE of less than 0.8, 0.1 and 0.3 for paprika: salt, pepper: salt and onion: salt compositions, respectively. In the case of partially mixed samples, repeatability studies were not performed as it was not possible to replicate partial mixing by shaking.

4.3 Results and discussion

4.3.1 Powder colour values and colour differences between powders

Digital colour imaging (DCI) methods use differences in colour values to assess mixture quality, thus there must be a difference in a colour value, such as ΔE , of the individual powders to be mixed. Table 4.1 presents CIELAB colour values obtained by DCI system (DigiEye) for the individual powders, the differences between them and also the colour values for well-mixed binary mixes. For all the binary mixes, there are differences in ΔE .

The largest is for paprika–salt at 73 and the smallest is for onion–salt at 5.6, thus it would be expected that the mixture quality for onion-salt would be the most difficult to assess, as the onion and salt have very similar colours.

The well-mixed paprika–salt mixes have ΔE colour values much closer to the paprika value than the salt value, which shows that paprika has a dominant effect on the ΔE value. ΔE progressively increases as the paprika content increases as expected.

Likewise, a similar trend was obtained for the pepper–salt mixes. The well-mixed onion–salt mixes also had ΔE colour values close to the onion, but there was no trend with increasing onion composition for the range presented and this suggests that it may not be possible to assess mixture quality of this mix using DCI.

Table 4.1- Colour values (CIELAB) and differences in colour (relative to white) for individual powders, and colour values for well-mixed binary mixes

Name of Sample	ΔE	a^*	b^*	L^*
Salt	4.70	-0.7	0.8	96.7
Paprika	77.7	35.2	39.0	33.7
Black Pepper	51.2	5.0	17.2	43.7
Onion Powder	10.3	-0.2	11.9	92.3
Difference [Paprika-Salt]	73	35.9	38.2	-63.0
Difference [Black Pepper-Salt]	46.4	5.7	16.4	-53.0
Difference [Onion-Salt]	5.6	0.4	11.1	-4.4
Well mixed Paprika-Salt [30:70]	64.9	29.7	29.3	41.4
Well mixed Paprika-Salt [50:50]	72.0	32.9	32.8	36.0
Well mixed Paprika-Salt [70:30]	75.3	33.7	35.0	33.7
Well mixed Black Pepper-Salt [30:70]	42.4	3.7	13.2	51.5
Well mixed Black Pepper-Salt [50:50]	47.7	4.3	14.5	46.4
Well mixed Black Pepper-Salt [70:30]	50.3	4.4	15.5	44.0
Well mixed Onion powder-Salt [30:70]	10.4	0.1	12.1	92.0
Well mixed Onion powder-Salt [50:50]	10.1	-0.2	11.6	91.4
Well mixed Onion powder-Salt [70:30]	10.4	-0.2	11.9	93.6

4.3.2 Mixture quality assessment using digital colour imaging

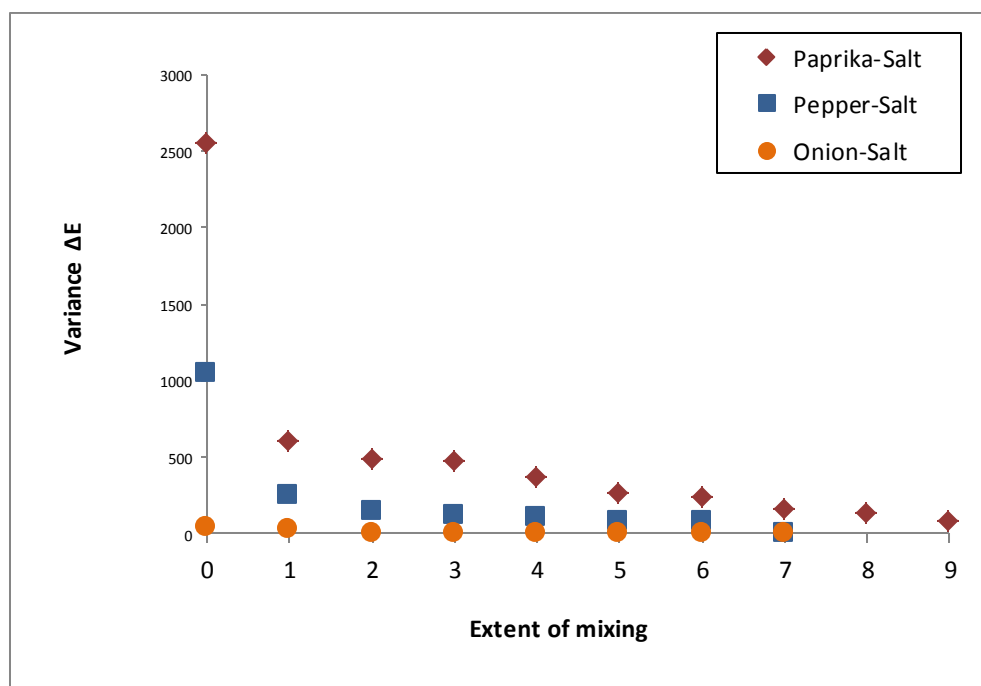
Data from the colour measurements for the three binary mixes as a function of mixing extent (or number of shakes) are presented for the 70% and 30% salt compositions in

Figure 4.2 and Figure 4.3, respectively. ΔE was measured for each of 25 squares [as illustrated in Figure 4.1] and variance ΔE was calculated using equation 2. The data is presented both as non-log and log plots for greater clarity. Figure 4.2a shows that the variance ΔE decreases rapidly upon shaking and that it is highest for paprika–salt and lowest for onion–salt, as expected from the values presented in Table 4.1. Data scatter was quantitatively estimated using the root mean square error of the linear regression of a log plot and these values are presented in Table 4.2. Figure 4.2b and Table 4.2 show that there is more scatter in the onion–salt data, suggesting that DCI may have greater difficulty in distinguishing colour differences for these components. There is less scatter for the other 2 mixes and there is a gradual reduction in variance ΔE as mixing progresses.

Table 4.2- Estimation of data scatter using the root mean square error of the linear regression of the logarithmic plots in Figure 4.2b, Figure 4.3b, Figure 4.6b and Figure 4.7b [The first data point (i.e. non-mixed powders) in each figure was omitted in the regression analysis]

	<u>25 squares</u>		<u>100 squares</u>	
	30% Salt	70% Salt	30% Salt	70% Salt
Paprika – Salt	0.76	0.51	0.97	0.93
Pepper – Salt	0.82	0.89	0.9	0.97
Onion - Salt	0.6	0.06	0.86	0.87

(a)



(b)

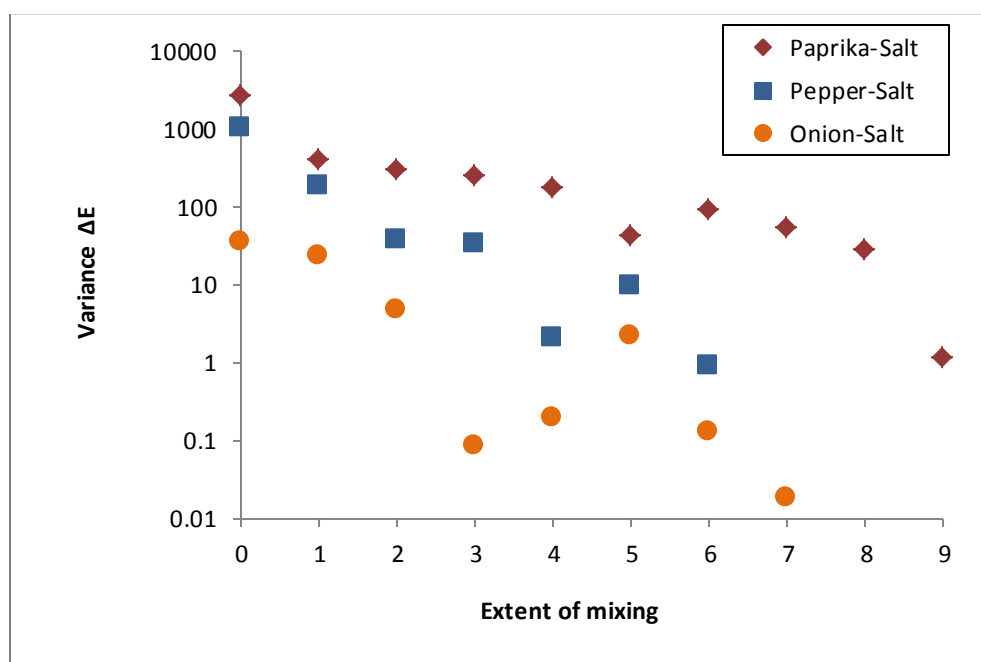
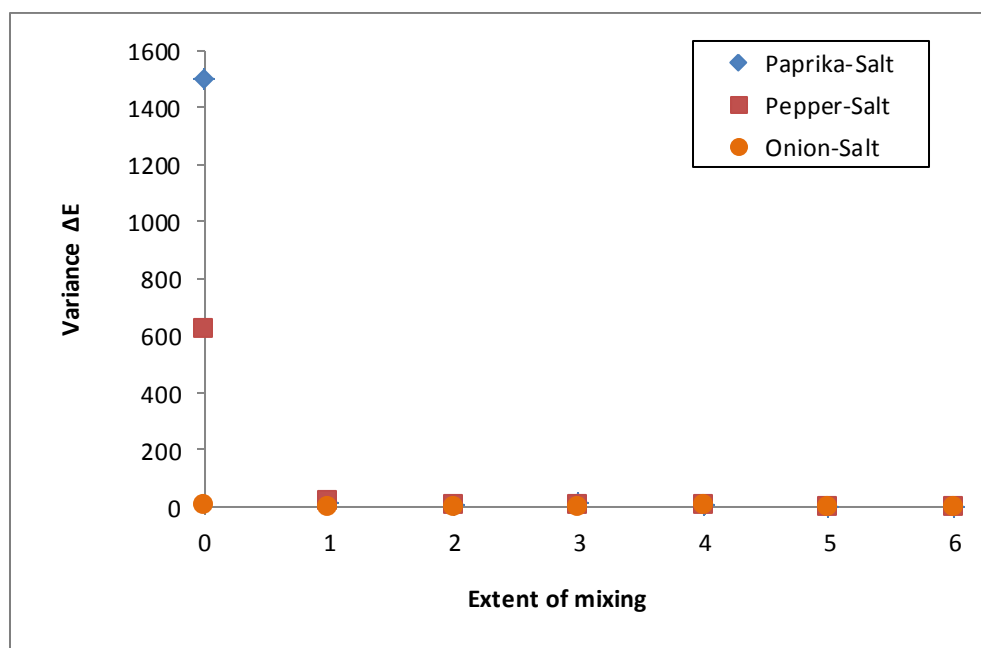


Figure 4.2- Variance ΔE [25 squares] for the three binary mixes as a function of extent of mixing for 70% salt concentration: a) non-log, b) log plot

Figure 4.3a shows the variance ΔE values for all mixes at 30% salt are a lot lower than their corresponding values for 70% salt [Figure 4.2]. Furthermore, Figure 4.3b and Table 4.2 show that the data for onion-salt is highly scattered at 30% salt content and suggests that DCI is unable to distinguish colour differences at this salt content. Overall, DCI has less capability for assessing mixture quality at the lower salt content.

(a)



(b)

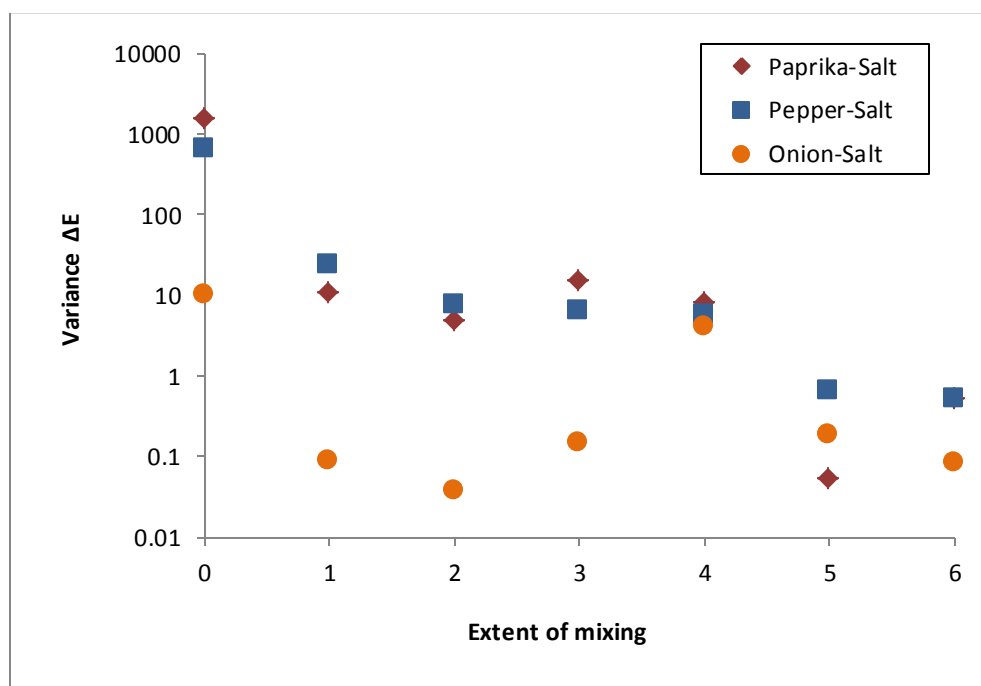


Figure 4.3- Variance ΔE [25 squares] for the three binary mixes as a function of extent of mixing for 30% salt concentration: a) non-log, b) log plot

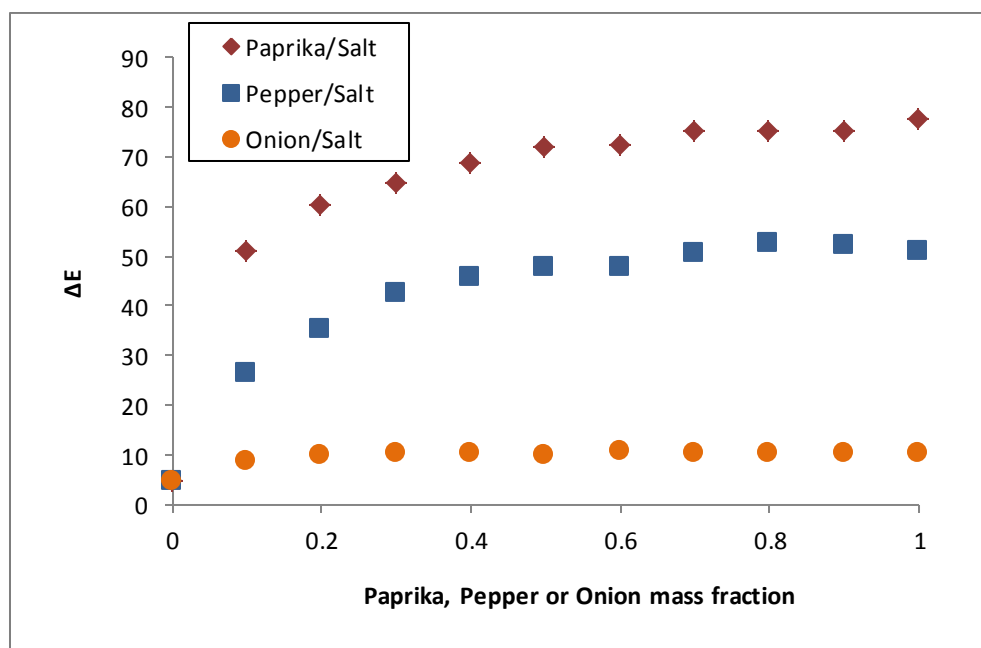
In Figure 4.2 and Figure 4.3 it is seen that for the 70% and 30% salt mixes the variance ΔE decreases with mixing extent for the paprika-salt and pepper-salt mixes as they approach a well-mixed state. However, at lower salt content the variance ΔE values were lower (Figure 4.3) which suggests that composition may influence the applicability of DCI. These data show a good potential for using DCI for assessing the mixture quality of these powders. It also shows that the approach may be limited if the difference in ΔE is too small.

4.3.3 Effect of powder composition on colour measurement

For a binary mix containing powders with different colours, one would expect to have colour variations in well mixed binary mixes containing different fractions of the components. Consequently, it might be expected that DCI should be able to differentiate between well-mixed mixes with different compositions. Trials were undertaken with binary mixes at 10% intervals between 0% and 100% salt for each of the binary mixes. Each mix was shaken several times until it was well-mixed. DCI was used to measure ΔE for each mix. Figure 4.4 shows how ΔE varies with % salt for each of the binary mixes.

For paprika-salt, there is an increase in ΔE over the entire concentration range; however the rate of increase in ΔE is much greater below 50% paprika. Consequently, the increase in ΔE becomes less sensitive as the paprika content is increased above 50%. Visual inspection of the well-mixed samples also showed that it was difficult to distinguish between paprika-salt mixes in the higher paprika concentration range. For pepper-salt, there was a gradual increase in ΔE up to about 80% pepper, after which this relationship did not exist which suggests that Digi-eye may not be able to detect concentration differences above 80%. The greatest rate of increase was below 50%. For onion-salt, there was only an increase in ΔE up to about 30% onion, after which the data was scattered. This suggests that DCI may not be able to or may have major difficulty in assessing the mixture quality of onion-salt mixes because the difference in ΔE is too small. This is in agreement with data presented in Figure 4.2 and Figure 4.3.

(a)



(b)

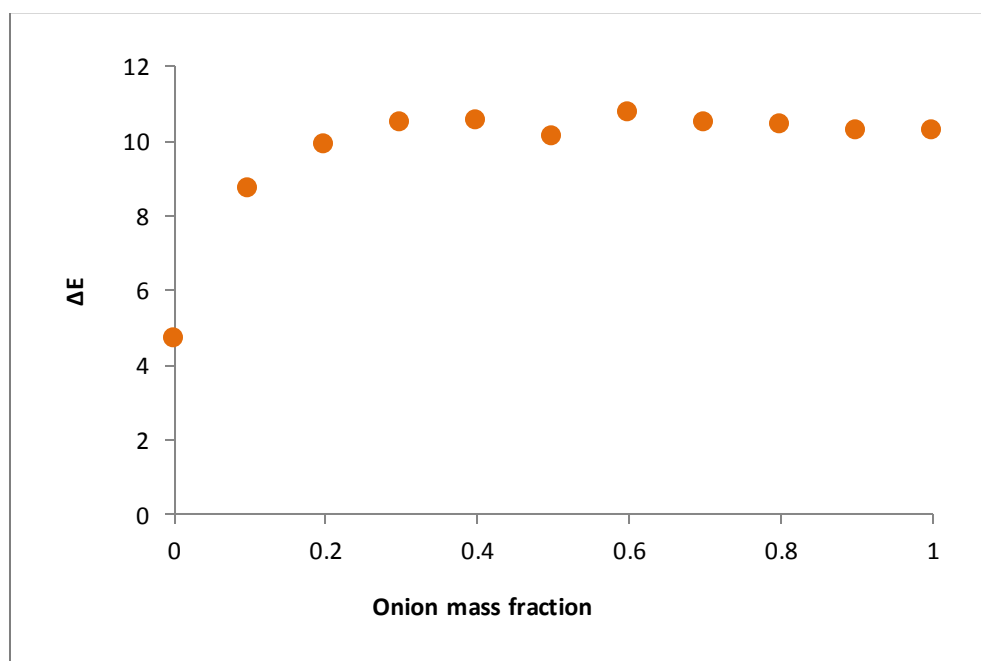


Figure 4.4- Effect of composition on ΔE of binary mixes: a) all mixes; b) onion-salt

In Figure 4.3, the variance ΔE of the pepper-salt mixes decreased more rapidly during mixing than the paprika-salt which may suggest that very good mixture quality was obtained much more rapidly in the pepper-salt trial. Furthermore, comparing data for pepper-salt and paprika-salt in Figure 4.2 and Figure 4.3 would suggest that very good

mixture quality was obtained in the 30% salt trials. However, this may be misleading because DCI has greater variance ΔE values for paprika-salt than pepper-salt and it has reduced detection capability for colour differences in the higher 70% paprika and pepper contents. So, the much more rapid improvement in mixture quality for both paprika-salt and pepper-salt may be erroneous because the results plotted may be due to DCI's lower colour difference detection capability above the 50% concentration range.

4.3.4 Effect of sample size on mixture quality assessment using DCI

A consequence of Figure 4.4 is that DCI may have major difficulty in assessing the mixture quality of, for example, pepper-salt mixes with high pepper content. This is because any colour deviations and corresponding variance that occur in the high pepper concentration range may not be detected. One approach to try and overcome this problem is to reduce the sample size. In powder mixing, variance depends on sample size; the variance increase as the size of sample reduces (Fitzpatrick, 2009). In the DCI procedure, the sample size is the size of the squares, thus reducing the size of the squares could potentially increase the variance. Reducing sample size will increase the variation in component concentrations between individual squares. This will increase variance ΔE , provided that some of the squares have concentrations within the concentration range where DCI has sensitivity.

To investigate the influence of sample size on the variance, trials were conducted with 50:50 mix of black pepper-salt. When sample size is reduced the number of pixels examined each time is also reduced. From Figure 4.5 it is seen that when the size of the squares is decreased i.e. the number of pixels is decreased from 34969 up to 4 the variance ΔE increases. Different number of samples were analysed for each image of 2*2 pixels size (in this case the number of samples equals to number of squares of size 2*2 pixels) and it was decided that 100 squares are sufficient to represent the mixture quality when 2*2 pixels were studied.

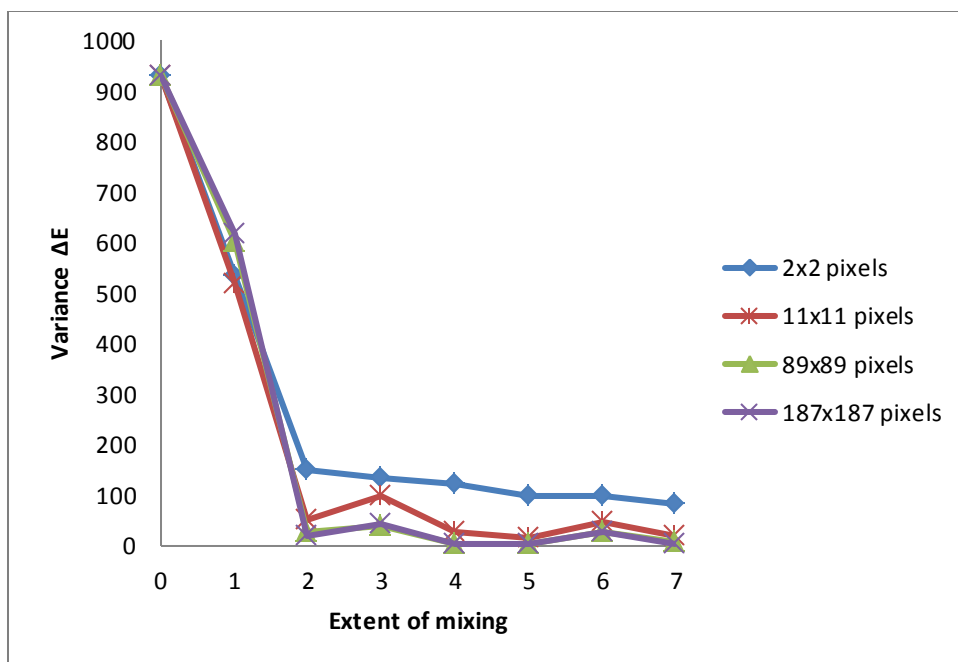


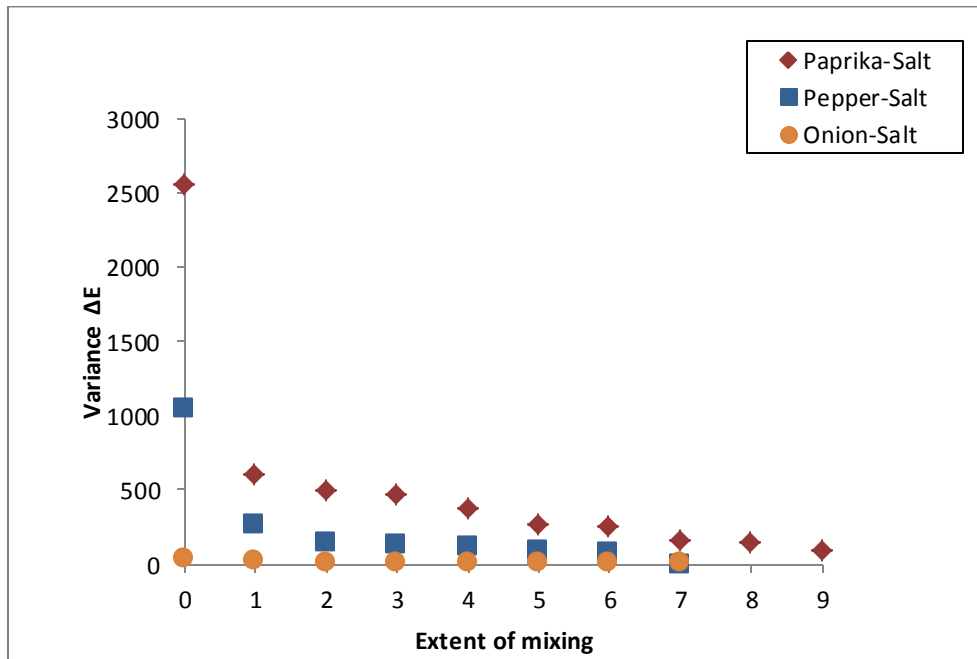
Figure 4.5- Effect of sample size (square size) for 50:50 Pepper-Salt mix

Consequently, trials were carried out with the binary mixes with a reduced sample size by increasing the number of squares in the colour image from 25 to 100, that is, a four-fold reduction in sample size. The data from these trials are presented in Figure 4.6 and Figure 4.7 for 70% and 30% salt contents, respectively. Figure 4.6 shows that higher variance ΔE values were obtained for smaller sample sizes (in comparison with Figure 4.2) and there was a much smoother reduction in variance ΔE during mixing with little data scatter (Table 4.2), even for the onion-salt mix. Figure 4.7 also shows higher variance ΔE values in comparison to Figure 4.3 and there is also a smooth gradual reduction in variance ΔE with little scatter (Table 4.2). For onion-salt, the variance ΔE rapidly reduces to a very low value and there is little difference between the values over most of the range. This is signifying that DCI may not be able to assess mixture quality for the lower salt content of 30%.

Figure 4.6 shows that DCI appears to be able to assess the mixture quality of the onion-salt mix at 30% onion content, even though Figure 4.4b would suggest it would have difficulty at this content. However, at the sample size used in Figure 4.6 there will be variation in onion content amongst the samples, thus some of the samples must have onion contents in the lower onion content range where DCI can distinguish colour differences. At 70% onion content, the probability of this occurring is a lot less and thus

the low variance values signify the lack of colour difference detection capability in this trial (Figure 4.7). Overall, reducing the sample size improved the ability for assessing mixture quality, even for the onion-salt powder mix.

(a)



(b)

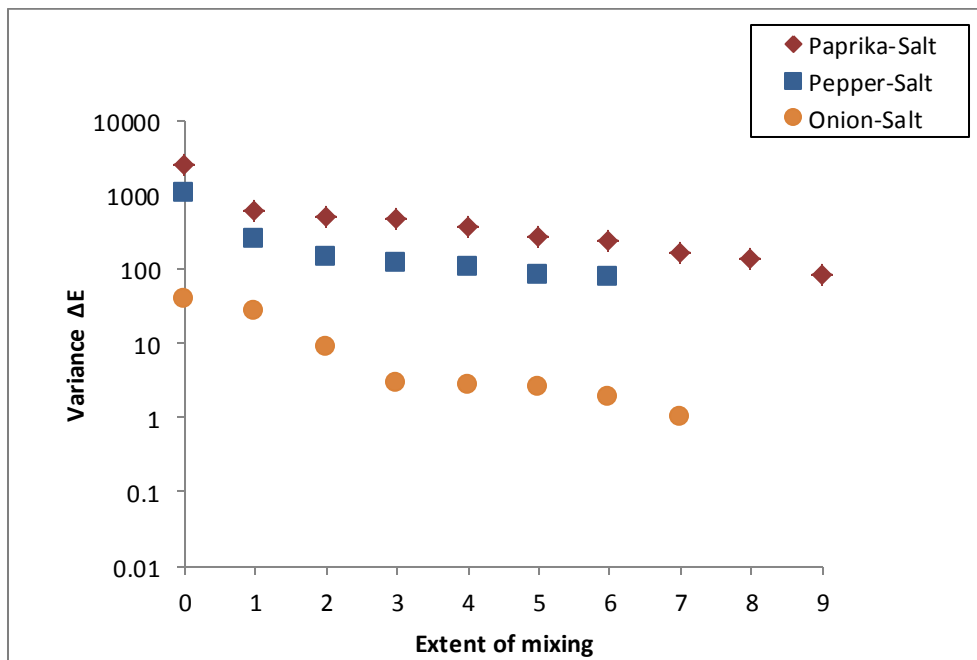
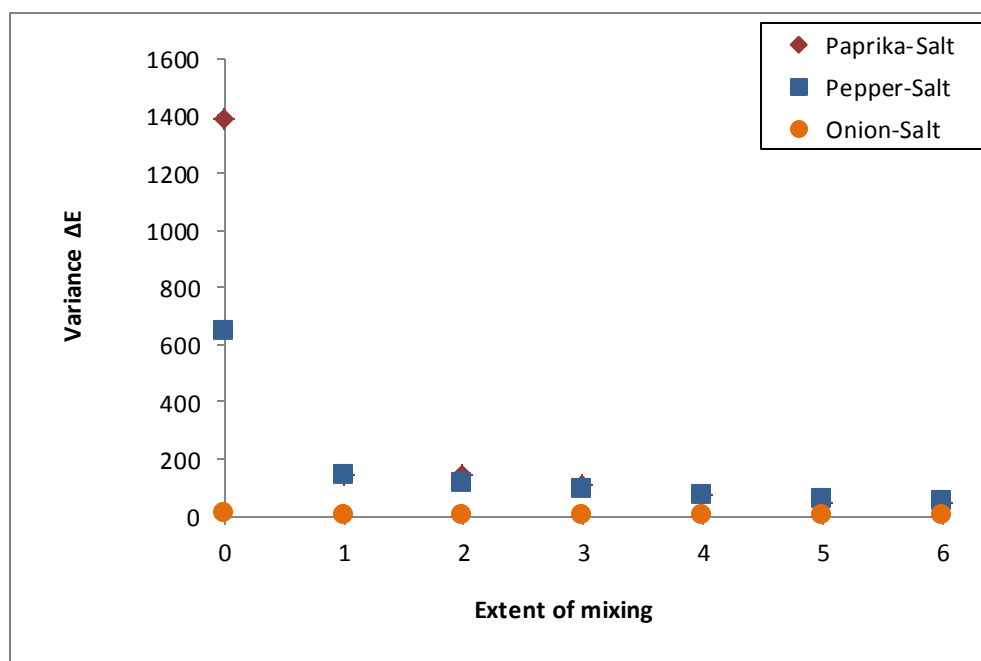


Figure 4.6- Variance ΔE [100 squares] for the three binary mixes as a function of extent of mixing for 70% salt concentration: a) non-log, b) log plot

(a)



(b)

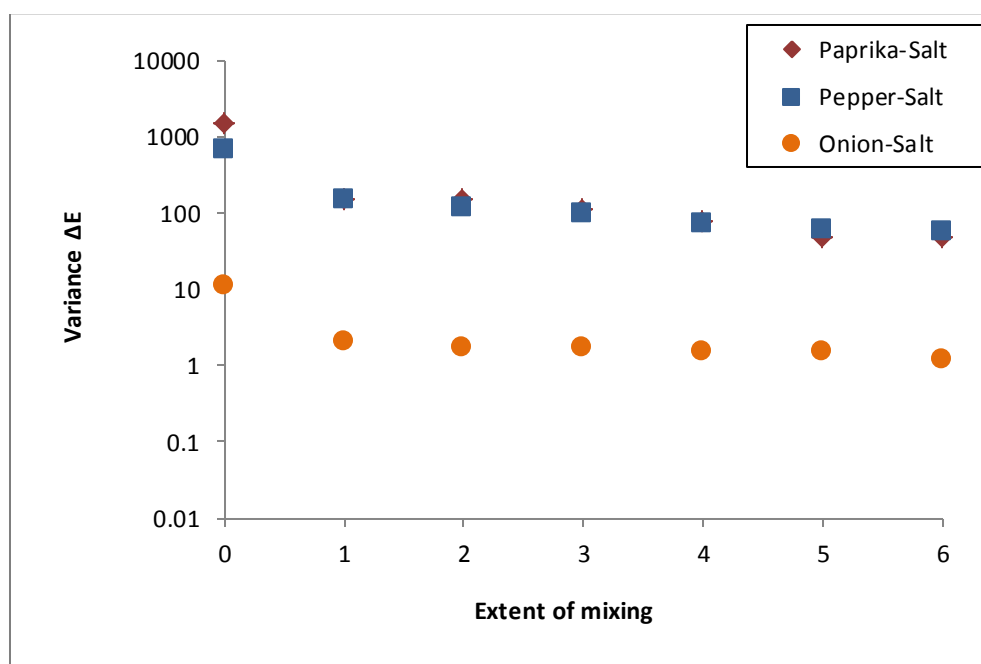


Figure 4.7- Variance ΔE [100 squares] for the three binary mixes as a function of extent of mixing for 30% salt concentration: a) non-log, b) log plot

4.3.5 Comparing mixture quality of different mixes using DCI

The mixture quality of different mixes cannot be compared based on comparing the values of variance ΔE . For example, Figure 4.6 shows that the variance ΔE for onion-salt is lower than that of paprika-salt. This does not signify that there is a superior mixture quality being achieved in the onion-salt mix. The reason for this is that it is not only mixture quality that influences the value of variance ΔE ; the difference in ΔE between the two component powders also has a major influence. This difference is much lower for onion-salt than paprika-salt and this is most likely the dominant reason why variance ΔE is lower for the onion-salt mixes.

4.3.6 Application of DCI and variance ΔE in quality control

DCI has potential for assessing the mixture quality of food powder mixes as a quality control tool. This is provided that there are sufficient colour differences between the component powders. In quality control, a representative sample would be taken and the variance ΔE would be measured. This measured variance ΔE would need to be compared to a limit variance ΔE below which the measured variance ΔE would be deemed to represent satisfactory mixture quality. A key aspect in this comparison is determination of the limit variance ΔE . This is a value that a processor would have to determine them self, for example by conducting a number of experimental trials. It is important to keep in mind that the sample size or number of pixels in the sample will influence the value of variance ΔE , thus this should be noted and kept constant. Furthermore cognisance must be given to other factors that could influence variability in the evaluation of variance ΔE , such as batch to batch variability in the colour of component powders and repeatability of the procedures used to evaluate variance ΔE .

4.4 Conclusions

Digital colour imaging (DCI) has potential for assessing the mixture quality of binary food powder mixes, provided that a colour difference can be measured between the powders. The greater the colour difference, the greater the potential for the DCI based approach. Even for powders with different colours, DCI may have difficulty in distinguishing between well-mixed samples with different compositions, however it is critical that there is a range of compositions in which DCI can distinguish, otherwise the technique will not work. Reducing the sample size, by reducing square size in the

images or reducing the number of pixels in a square, can help improve the colour variance approach for assessing mixture quality.

CHAPTER 5

DRY MIXING OF FOOD POWDERS: EFFECT OF WATER CONTENT AND COMPOSITION ON MIXTURE QUALITY OF BINARY MIXTURES

This work studied the effect of composition of powders and water content on mixture quality (MQ) of three binary powder mixtures – paprika/salt, oregano/salt and sugar/salt that had significant differences in mixability. Furthermore, the powder flow behaviour of the individual ingredients at various moisture contents was investigated. The mixing behaviour was assessed using coefficient of variation (CoV). Salt compositions were varied from 80 % down to 0.5 % (w/w) concentration in the mix .To study the effect of water content, the paprika and oregano were preconditioned at different humidities in the range of 37 to 94%. Results showed that sugar / salt and paprika / salt displayed much better MQ than the oregano / salt mix. Water content affected the mixing behaviour. When paprika with high a_w was mixed with salt, the time required to reach good MQ increased. On mixing oregano with high a_w with salt there was an improvement in the MQ.

5.1 Introduction

Dry mixing is a process that is widely used in many types of industries such as manufacture of ceramics, plastics, fertilizers, detergents, pharmaceuticals and food & animal feed production (Barbosa-Cánovas et al., 2005b; Cooke et al., 1976; Fan et al., 1990). Mixing is an important step for the food industries to produce products with constant properties and to obtain uniformity in different properties such as color, texture, taste and concentration. Most of the industrial food mixing processes are batch. Knowledge of mixing is a combination of science and 'know-how' which is preserved by the large food companies (Barbosa-Cánovas et al., 2005b, c). Solid mixing is a complex process which is influenced by the particle shape and particle size distribution as well as the flow characteristics of the powders (Fan et al., 1990; Sommer, 2000). Since food materials are organic in nature these properties exhibit more variation (Barbosa-Cánovas et al., 2005c). In powdered systems properties can also vary during the mixing and hence it is more difficult to evaluate and define mixing for particulates and powders than it is for fluids (Barbosa-Cánovas et al., 2005b).

A common industrial problem with powders is their failure to discharge reliably from bins, silos and hoppers as well as their insufficient or unpredictable flow in feeders, dosing and packing machines. These problems occur due to the powder's flow behaviour and often cause adverse interruptions in the production processes. Moreover, different flow properties of constituent powders in mixes may cause variations in mixture homogeneity, which in turn may lead to pack weight, performance, sensory properties and quality differentiations in the products. Powder flowability is related to the movement of powder particles and thus influences powder mixing. Storage conditions and powder properties may influence the flowability of powders and thus their mixing. Particle size affects the flowability of powders (Fitzpatrick et al., 2004); the smaller the particle size, the greater is the contact area and intermolecular forces between the particles which tends to make the powders more cohesive (Landillon, 2008) and potentially more difficult to mix. Powder moisture content also affects the flowability; increased moisture content tends to reduce flowability due to the formation of liquid bridges and capillary forces between the particles (Fitzpatrick et al., 2007; Fitzpatrick et al., 2004; Scoville and Peleg, 1981). According to Fitzpatrick et al. (2004) the effect of moisture content and particle size on

the powder flowability may be coupled. Since mixing is a process where two or more powders are dispersed by random movement of particles (Fan et al., 1979) it is important that the powders being mixed can move easily throughout each other. However, ease of motion may also induce segregation mechanisms due to differences in particle size and powder densities.

Powder mixing ratio can also impact the mixing characteristics of powders. Kuakpetoon et al (2001) showed that when three different compositions of soft wheat flour and hard wheat flour were mixed it was observed that the one with equal quantities of both types of flours required the longest mixing time. This could be attributed to the high variation in particle size of the powders used. Similarly the effect of concentration of powders on segregation tendency of a sugar:starch mixture was studied by Barbosa-Canovas et al (1985) where different recipes (75%, 50% and 25% by weight) of sugar:starch mixtures were exposed to 10 minutes of vibration at different speeds to induce segregation in the mixture. From these experiments it was seen that concentration played a crucial role in segregation tendency of the powders and it determined the availability of surfaces for particle interactions to take place. The industrially manufactured food powder mixes usually consist of different amounts of multiple components that vary widely in their properties, this can cause segregation tendency in the mixture (Clarke and Berry-Ottaway, 1970). However according to Devriendt et al (2013) the tendency to segregate is lesser in multicomponent mixtures because the mobility of particles is lower and hence the effect of the collective behavior of similar natured particles is reduced unlike in binary mixtures. Thus, in order to gain a better understanding of mixing / segregation mechanisms, binary powder mixtures were analyzed in this study. Different binary mixtures that differ in mixability were produced by mixing them in a prototype lab-scale paddle mixer. The objective of this study was to investigate the influence of mixture composition and water content of the powders on mixing and mixture quality of binary food powder mixes. Furthermore, powder flowability of the mixture's constituents at various moisture contents were measured, as this may influence powder mixing.

5.2 Materials and Method

5.2.1 Powders and binary mixes

Four food powders, paprika, oregano, sugar and salt, were obtained from Santa Maria AB, Sweden. The binary powder mixes prepared were:

- Paprika – Salt (P/S)
- Oregano – Salt (O/S)
- Sugar / Salt (S/S)

5.2.2 Powder properties

The median particle size (D_{50}) for salt, paprika and sugar was measured using the Malvern Mastersizer 2000. Sieve analysis was used to measure the median particle size of the oregano because its size could not be measured using the Mastersizer. Poured and tapped bulk density was measured by pouring a known mass of powder into a graduated cylinder and reading off the powder volume. The measured powder property values for these powders are presented in

Table 5.1.

Table 5.1- Powder property data

Powder	Median Particle Size (μm)	Particle Density (kg L^{-1})	Poured Bulk Density (kg L^{-1})	Tapped Bulk Density (kg L^{-1})
Salt	435	2.16	1.28	1.40
Paprika	225	1.36	0.45	0.52
Oregano	1600*	1.21	0.07	0.07
Sugar	542	1.59	0.86	0.95

5.2.3 Mixture compositions

The following salt compositions were mixed for the binary mixes: 0.1 %, 0.5%, 1 %, 20 %, 50 %, 80 % (w: w). The powders were stored in air tight containers at 30 %RH and 20 °C to ensure that the original moisture content of the powders did not vary. For each

type of binary mixture produced depending on the composition and type of powder used in the mix the total quantity of powders used inside the mixer varied so that the mixer had sufficient amount of powder for mixing. Table 5.2 shows the quantity of powders used for the different mixing trials.

Table 5.2- Quantity of Powders for different binary mixtures and their compositions

Composition (%w/w)	Total mass of Paprika:Salt mix (g)	Total mass of Oregano:Salt mix (g)
1:99	2000	600
20:80	2000	600
50:50	2000	300
80:20	1000	300
99:1	1000	300

From Table 5.2 it can be seen that in case of P/S mixes when the salt concentration was equal to or more than 50% by weight in the binary mix the mass used was double the amount (2kg) as compared to those with lower amounts of salt. Similarly, in case of O/S mix the total mass of powders inside the mixer was 600g when the amount of salt was higher than 50% by weight as compared to 300g for when salt concentration was lower. Such big difference in the total mass of powders used inside the mixer is due to the large variations in the bulk densities of the powders used. Oregano has very low bulk density (Table 5.1) and thereby the total mass of the powder mix inside the mixer is drastically reduced. In order to cover the blades of the mixer and get sufficient powder for mixing, the total mass for each type of binary mix had to be specifically chosen so as to enable mixing for different compositions.

5.2.4 Powder conditioning

To study the effect of higher water content in paprika, oregano and salt, the powders were pre-conditioned at different humidities ranging from 40 to 95%RH and were

mixed at 50:50 (w:w) ratio. Salt was pre-conditioned only upto 74%RH. The powders were placed as a thin layer on a steel tray inside a climate chamber (Vötsch Industrietechnik GmbH VCL4010) with the required humidity setting and depending on the humidity to be achieved the duration used for conditioning varied between 24 h – 72 h. The powder bed was sampled across different points and water activity was measured using Aqua Lab 4TE Dew point water activity meter to check if the required value had been reached.

5.2.5 Water sorption isotherms

The isotherms were determined for paprika and oregano powders by conditioning them at a number of different relative humidities in the climate chamber. The powders were placed inside small cups in the climate chamber for approximately 24 h – 36 h depending on the humidity to be reached and they were then sealed using the lids and parafilm tape and placed overnight in a refrigerator so that the water activity was equilibrated within the powder mass. In case of higher humidities, such as 90%RH, the duration for conditioning was increased to around 48 h for paprika powder. The water activity of the powders were measured and then they were oven dried for 24 h at 70 °C in a Gallenkamp vacuum oven and the moisture content was evaluated using the equation 1,

$$\%Moisture\ content = \left(1 - \frac{w_f}{w_i}\right) * 100 \quad (1)$$

5.2.6 Determination of flow properties

The flow properties of powders may influence mixing and mixture quality thus the flow functions of paprika, oregano and salt were determined with the use of a Powder Flow Tester (PFT) from Brookfield Engineering Laboratories Inc. which complies with the test procedure ASTM D6128 using the annular and Jenike shear tests techniques. The powder flow function is a plot of the unconfined failure strength versus the major principal consolidation stress. A vane lid was used in the measurement of the flow function of the powders. The flow function tests were undertaken using the 263 cc volume shear cell and running the standard flow function test program. This program measures the flow properties over the range of five major principal consolidation

stresses in a geometric progression that generates values of about 0.6, 1.2, 2.5, 5.0 & 10 kPa. PFT was connected with a PC provided with Powder Flow Pro V1.2 software. The flow functions of paprika, oregano and salt are presented in Figure 5.1 (the results represent the average values of three independent measurements). The three powders display different flow functions with salt being free flowing, paprika being easy flowing and oregano being cohesive. The oregano may be a little deceptive in the sense that its cohesiveness may be due to mechanical interlocking under compaction due to its large particle size and irregular leafy shape.

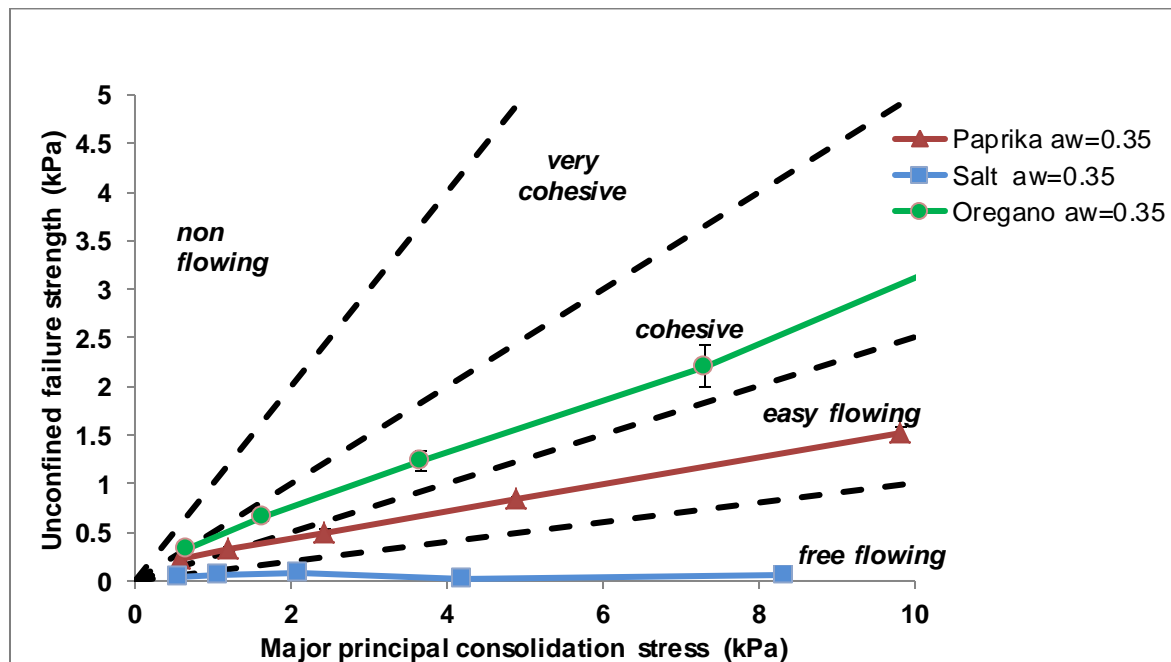


Figure 5.1- Flow function for paprika, oregano and salt at $a_w = 0.35$

5.3 Results and Discussion

5.3.1 Mixture quality of paprika / salt, oregano / salt and sugar / salt

The mixing curves for paprika / salt (P/S), oregano / salt (O/S) and sugar / salt (S/S) at 50 % salt contents are presented in Figure 5.2. These curves show that the MQ of S/S is very good being at 0.03 CoV or less for all mixing times except the first, thus S/S is very easy to mix. P/S also mixed very well although it was not as easily mixed as S/S. P/S and S/S had a lot better MQ than that of O/S. Visual inspection showed that the S/S and P/S appeared well-mixed, while there was an obvious segregation occurring in the O/S, with

more salt flowing towards the bottom and more oregano floating towards the top. The salt appeared to sieve its way down between the leafy oregano particles. From Table 5.1, it can be seen that sugar and the salt have the closest size and density values, while the oregano has a much larger particle size and lower bulk and particle densities. In fact the bulk density of oregano is very low, thus there exists large voidage between the oregano particles for the salt particles to fall down through. This segregation tendency can be explained by the differences in size and densities since lighter oregano particles float to the top on vibration (Graversen, 2012) and the salt particles sieve towards the bottom through the large voids between the leafy shaped oregano particles.

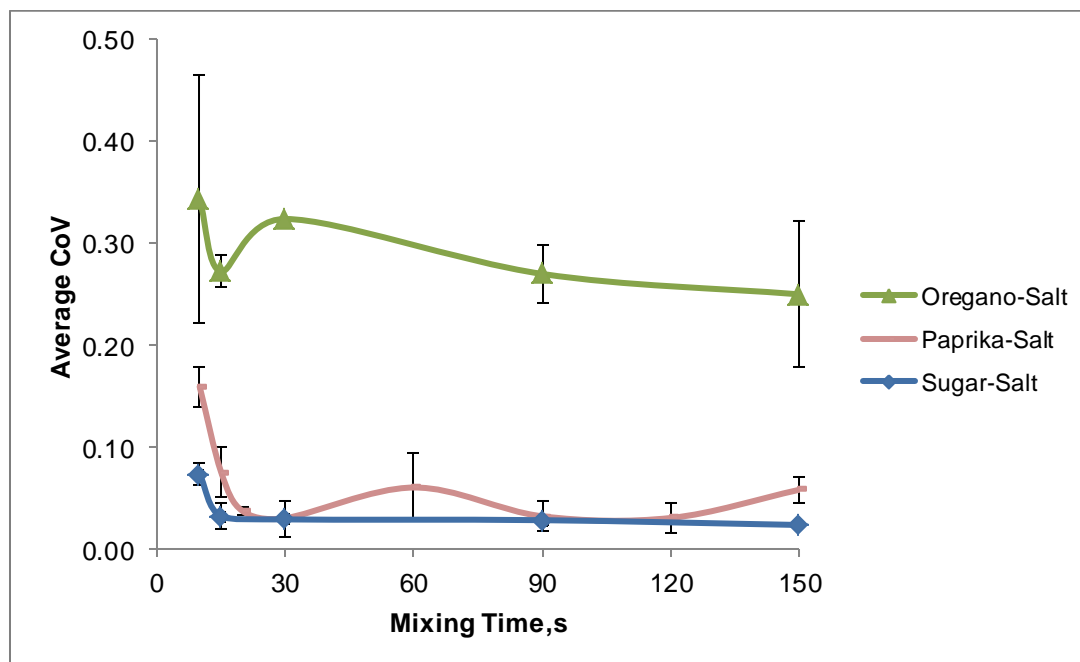


Figure 5.2- Mixture quality of paprika/salt, oregano/salt and sugar/salt mixes at 50% compositions

5.3.2 Effect of mixture composition

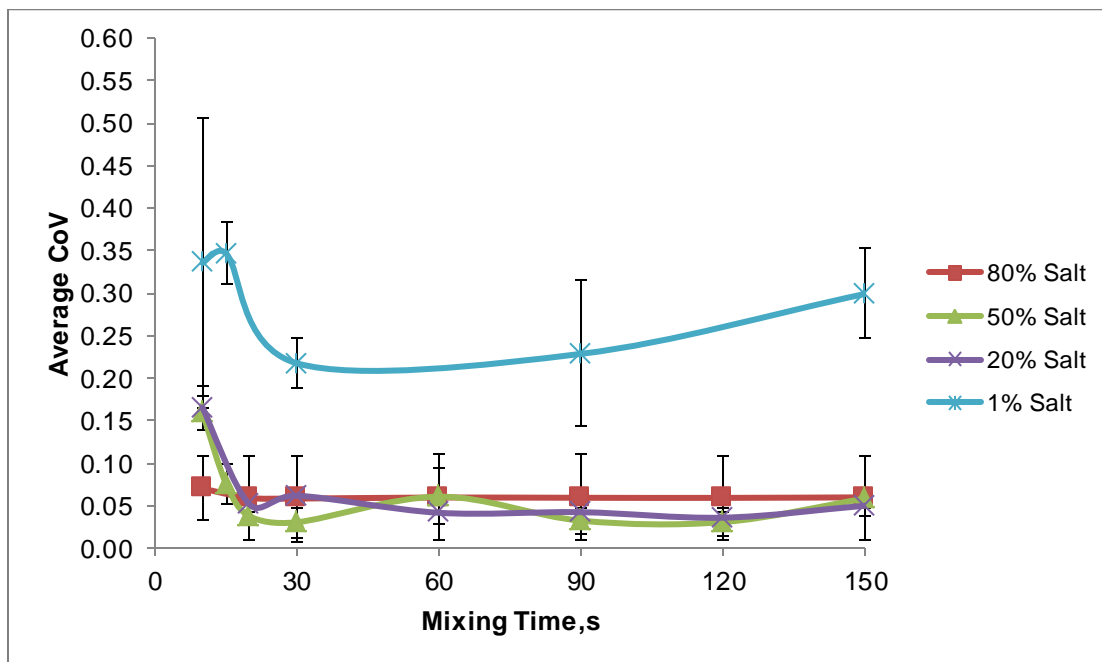
Figure 5.3a illustrates the effect of composition on MQ for P/S in the range of 1 – 80 % salt, and Table 5.3 provides average CoV values at the end of mixing. The CoV values obtained in the range of 20 to 80% salt were very similar and were less than or equal to 0.06 (which can be considered as well-mixed), thus mixture composition is not affecting the MQ of P/S in this range. At 1% salt, there was a reduction in mixture quality highlighted by a significant increase in CoV.

Figure 5.3b and Table 5.3 provide data on the effect of composition on the MQ of O/S mixes. These data show that there is a progressive dis-improvement in MQ as salt content is reduced (or oregano content is increased), as highlighted by the higher CoV values. This may be expected because there are more void spaces between the particles as oregano content increases due to its very low bulk density, which allows more space for salt particles to sieve their way downwards, thus facilitating the segregation tendency of salt from oregano.

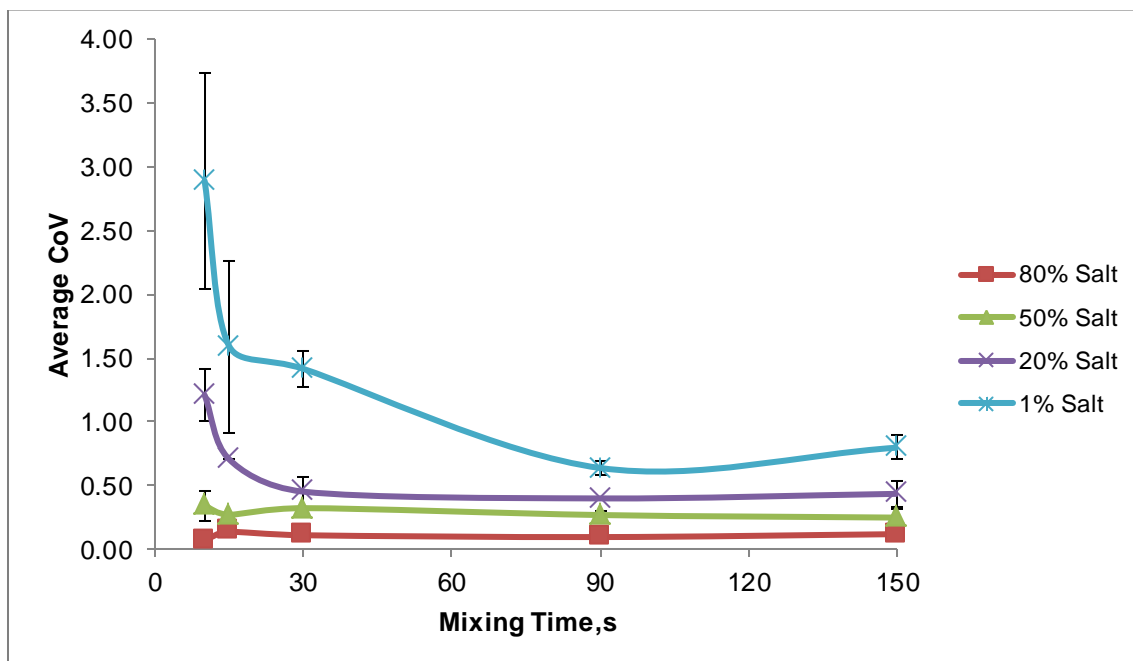
In the above trials, MQ was worst at the lowest salt content of 1 % for both P/S and O/S, which suggests that composition will influence MQ at the extremes of composition. Consequently, further trials were conducted at lower salt contents of 0.5 % and 0.1 % salt for both mixes. The results from these trials are provided in Figure 5.3c and Table 5.3. They show that the MQ, as assessed by CoV, dis-improves further for both mixes as the salt content is reduced, although there is very large variability in the values for the replicates as indicated by the error bars. This variability may be expected due to the low number of salt particles present at the sample size at the low salt concentrations (e.g. it can be estimated that there are about 20 median sized salt particles in a well-mixed 2 g sample at 0.1% salt content).

The above results suggest that the influence of composition on MQ is greater for powders that are more difficult to mix. Consequently, additional trials were conducted on a S/S mix, which is very easy to mix and even easier than P/S (Figure 5.2). Table 5.2 shows that very good mixing was achieved for S/S even down to 1% salt where the CoV was 0.08. At lower salt concentrations, the MQ dis-improved but it was still superior to P/S (Figure 5.3c). Overall, the results show that composition may influence the MQ of the mix, especially at low concentrations of salt, although this will be influenced by how easy the powders are to mix. Composition has a greater influence on the MQ of powders that are more difficult to mix, such as O/S.

(a)



(b)



(c)

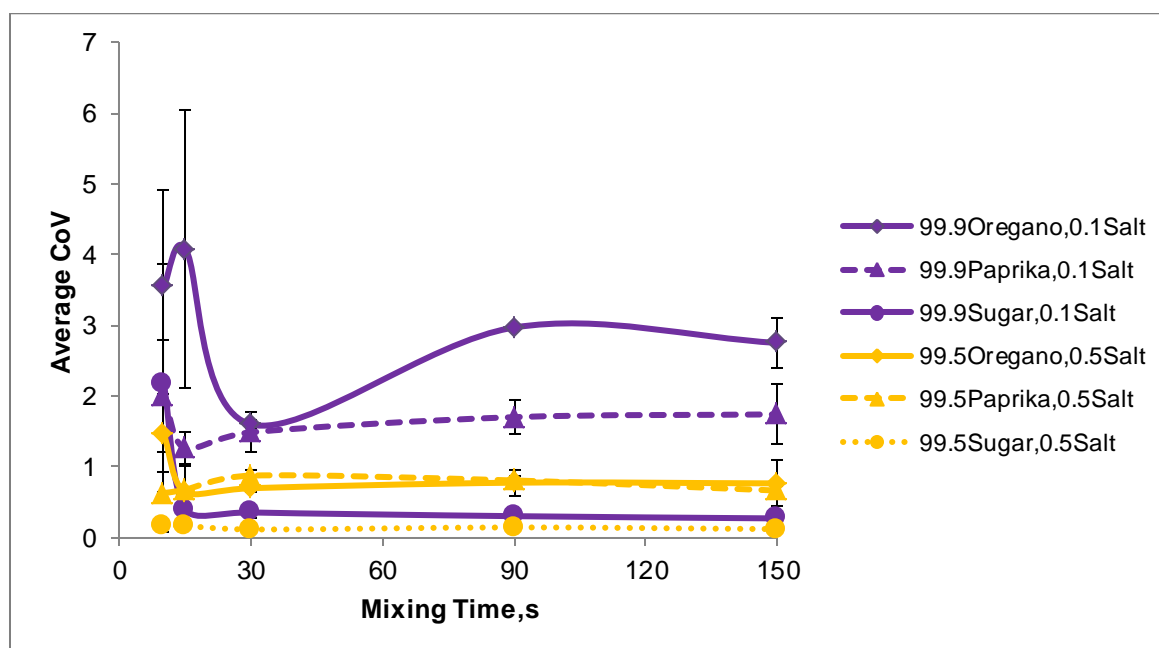


Figure 5.3- Effect of composition on mixture quality of (a) paprika / salt and (b) oregano / salt (c) effect of low concentrations of salt on P/S, S/S and O/S

Table 5.3- Influence of composition on the co-efficient of variation values at the end of mixing (150 s mixing time) for paprika / salt (P/S), oregano / salt (O/S) and sugar / salt (S/S) mixes

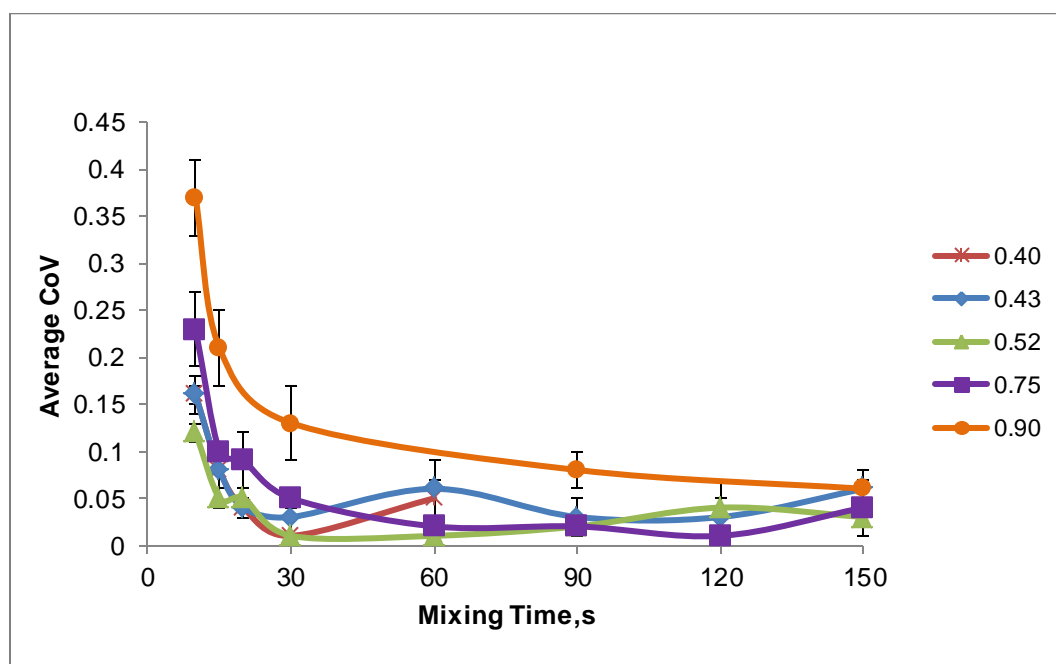
Powder Mix	Salt content (%w/w)					
	80	50	20	1	0.5	0.1
P/S	0.06	0.06	0.05	0.30	0.66	1.74
O/S	0.12	0.25	0.44	0.8	0.76	2.75
S/S	-	0.02	-	0.08	0.12	0.27

5.3.3 Effect of water content of paprika

Paprika and salt were mixed at a ratio of 50:50 by weight. The salt was maintained with $a_w < 0.70$, which is below the critical relative humidity of NaCl at around 0.75, thus the salt had very low water content. The paprika was conditioned to achieve a_w values in the range of 0.4 to 0.9. The conditioned powders were mixed with salt in the paddle mixer

and the influence of a_w on MQ is illustrated in Figure 5.4a. It can be seen that paprika powders with a_w values in the range of 0.4 to 0.75 had little effect on MQ. However, at $a_w = 0.9$ the MQ was affected, as the MQ improved more slowly over the mixing time than the other mixes, although it did move towards the same final values of the other mixes. The rationale for this behaviour is most likely due to the increased cohesion due to major uptake of water by the paprika powder at $a_w = 0.9$. Water sorption isotherm data is plotted for paprika in Figure 5.5. The water content of paprika at $a_w = 0.9$ is around 30% while it is around 15% at $a_w = 0.75$. This increase in water content most likely increased the cohesion of the powder making it more difficult to mix the powders. The influence of water activity on the flow behaviour of paprika was determined using the PFT tester. The water activity ranged from 0.15 to 0.9. Flow functions within this range are presented in Figure 5.9a. Water activity had a major influence on the flow function with higher water activity progressively moving the paprika from easy flow to cohesive and to highly cohesive. At a_w of 0.9, the paprika was classified as very cohesive and thus making it more difficult for the paddle mixer to obtain good MQ. The presence of water leads to the formation of liquid bridging and strong capillary forces between the powders thereby making them more cohesive and more difficult to mix (Kuakpetoon et al., 2001; Palzer and Sommer, 2011; Teunou et al., 1999). Figure 5.4b compares the influence of a_w at 0.58 and 0.9 for 20% and 80% paprika contents. The 80% paprika mix shows a similar trend to the 50% insofar as the paprika at $a_w = 0.9$ is more difficult to mix. For 20% paprika content the MQ was very good even when the paprika had high $a_w = 0.9$. Therefore it shows that the greater the paprika content at $a_w = 0.9$, the more difficult the mixing, which is to be expected due to the increased cohesion from the greater content of paprika.

(a)



(b)

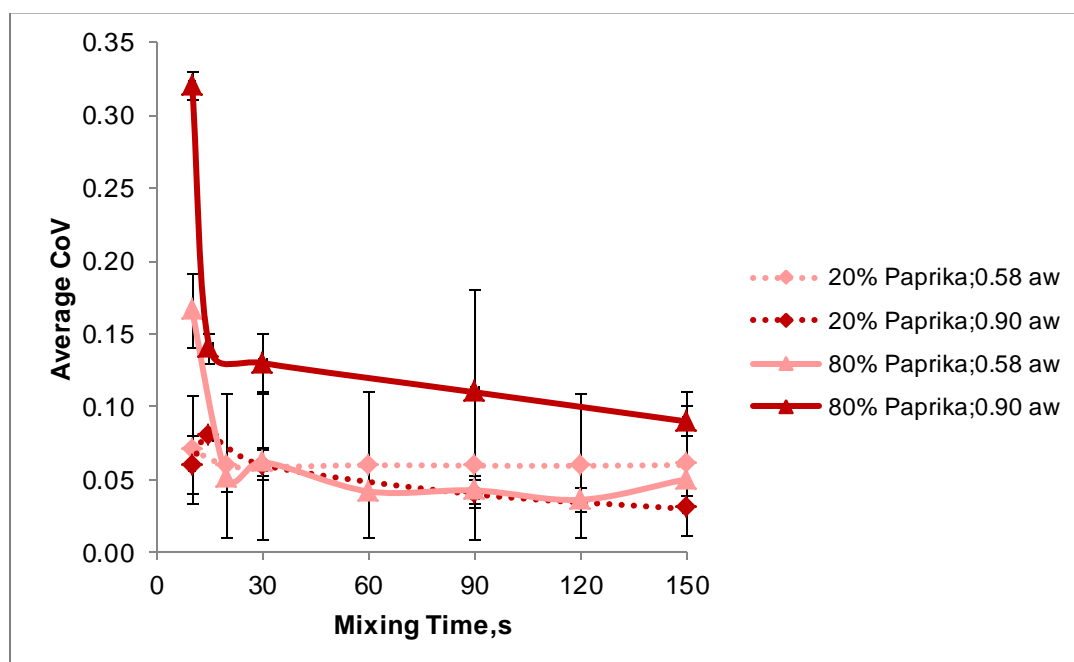


Figure 5.4- Effect of a_w on the mixture quality of paprika / salt: (a) 50% paprika, (b) 20% and 80% paprika

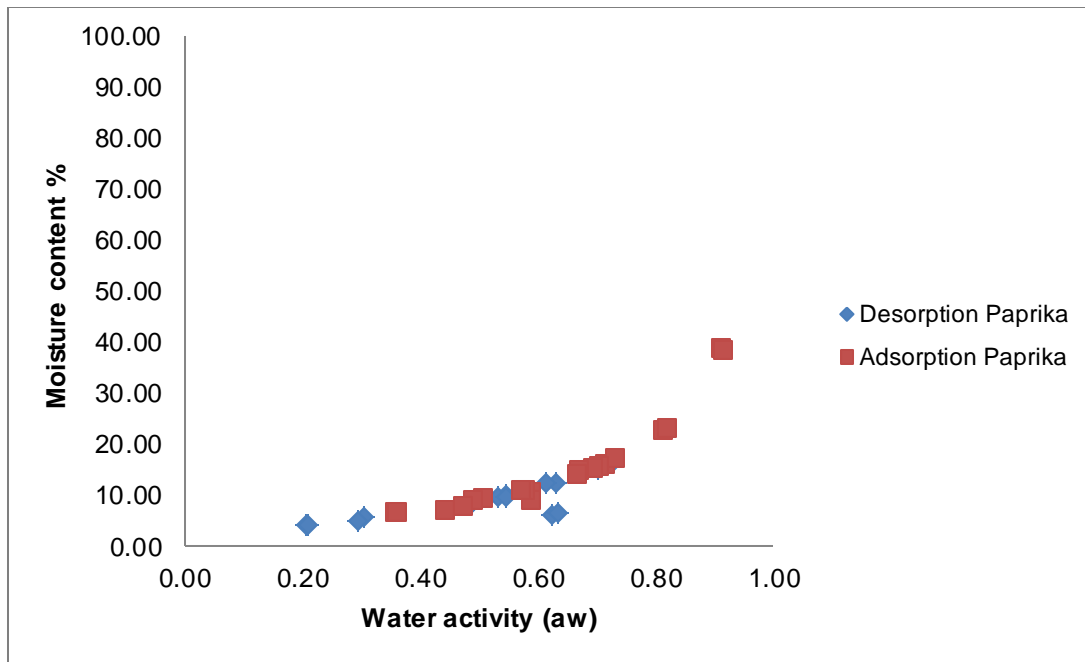


Figure 5.5- Water sorption isotherm for paprika (20°C)

5.3.4 Effect of water content of oregano

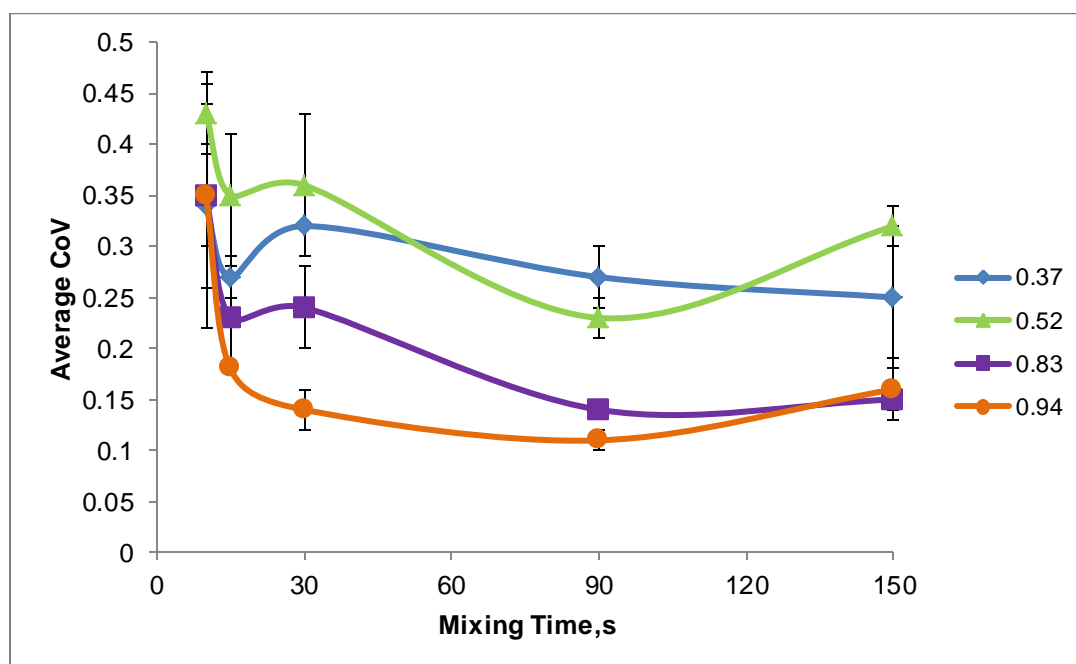
A similar set of mixing trials were carried out with oregano and salt. Initially, they were conducted at an oregano : salt ratio of 50 : 50 by weight and the salt was maintained at an $a_w < 0.7$. The oregano was conditioned to a_w values in the range of 0.37 to 0.94. The influence of a_w on the MQ of the mixes is presented in Figure 5.6a. The behaviour is quite different to that of paprika / salt, in so far as increasing a_w caused an improvement in mixing and the MQ attained, especially at the higher a_w values of 0.82 and 0.94.

In section 5.3.1, it is shown that oregano and salt did not mix well and segregation was observed whereby oregano particles moved to the top and salt to the bottom. The improvement in mixing at higher a_w was most likely due to moisture sorption by the oregano particles which made them more cohesive and sticky. Coelho and Harnby (1979) reported that when granular or spherical particles uptake moisture there is a significant improvement in the MQ. Water sorption isotherm data is presented for oregano in Figure 5.7. The water content of oregano at $a_w = 0.9$ is around 20% while it is around 10% at $a_w = 0.5$. The influence of water activity on the flow behaviour of oregano was determined using the PFT tester and the flow functions are presented in Figure 5.9b. Water activity in the range of 0.13 to 0.56 had no influence on the oregano

flow function, however the oregano flow function became more cohesive at $a_w = 0.82$. Visual inspection showed that at $a_w = 0.82$ and 0.94 the oregano particles were coated by many salt particles. This is because the presence of moisture inhibits the movement of individual particles (Kuakpetoon et al., 2001) and helps them to bind together forming cohesive bonds between the oregano and salt particles. Pasha et al (2014) reported that one approach to reducing the segregation tendency of a binary mix of small and large sized particles is to increase the stickiness of the large particles so that the small particles stick to it. On further visual observation of the oregano / salt mixing process it was evident that the mixing improved at the higher water content as vertical segregation of the oregano to the top and salt to the bottom was reduced.

Additional mixing trials were carried out at $a_w = 0.45$ and 0.9 for oregano contents of 20% and 80%. The results from these trials are presented in Figure 5.6b. The effect of the higher a_w on mixing and mixture quality at 80% oregano is very similar to that at 50%, that is, there is a major improvement in mixing. However, at the lower 20% oregano content, the influence of higher a_w was not significant, thus improvement in mixture quality depends on the oregano content in addition to the high water activity.

(a)



(b)

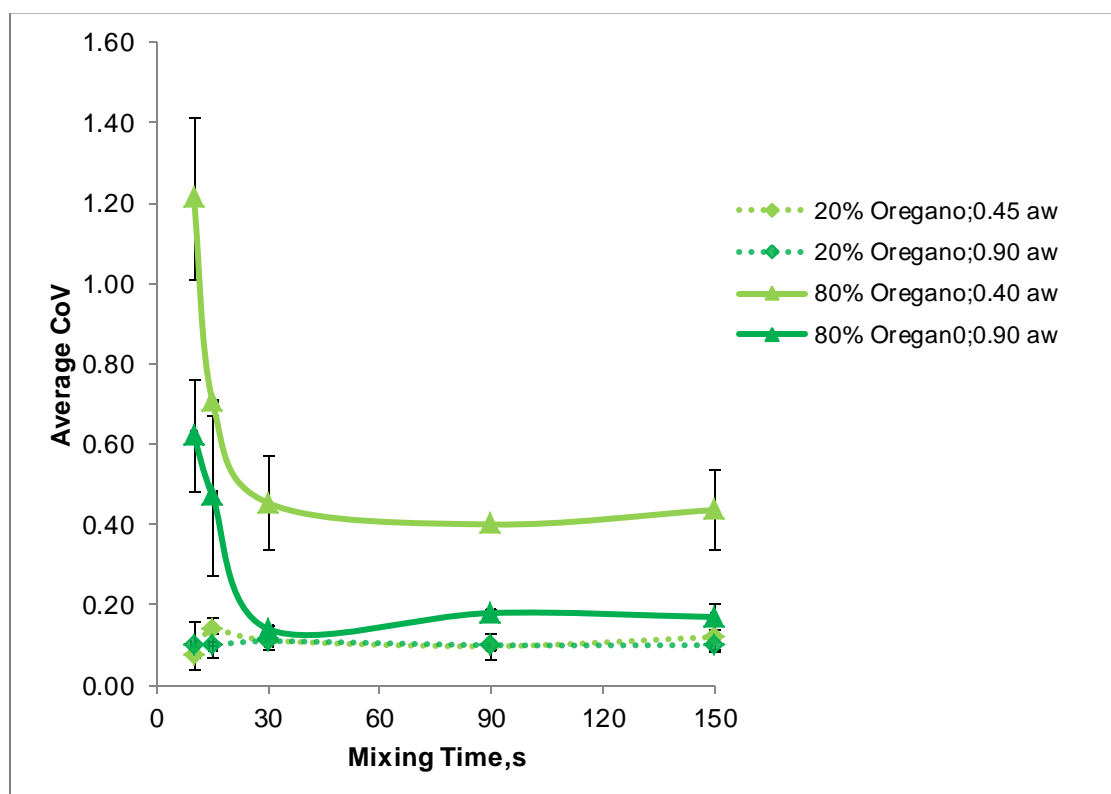


Figure 5.6- Effect of a_w on the mixture quality of oregano / salt: (a) 50% oregano, (b) 20% and 80% oregano

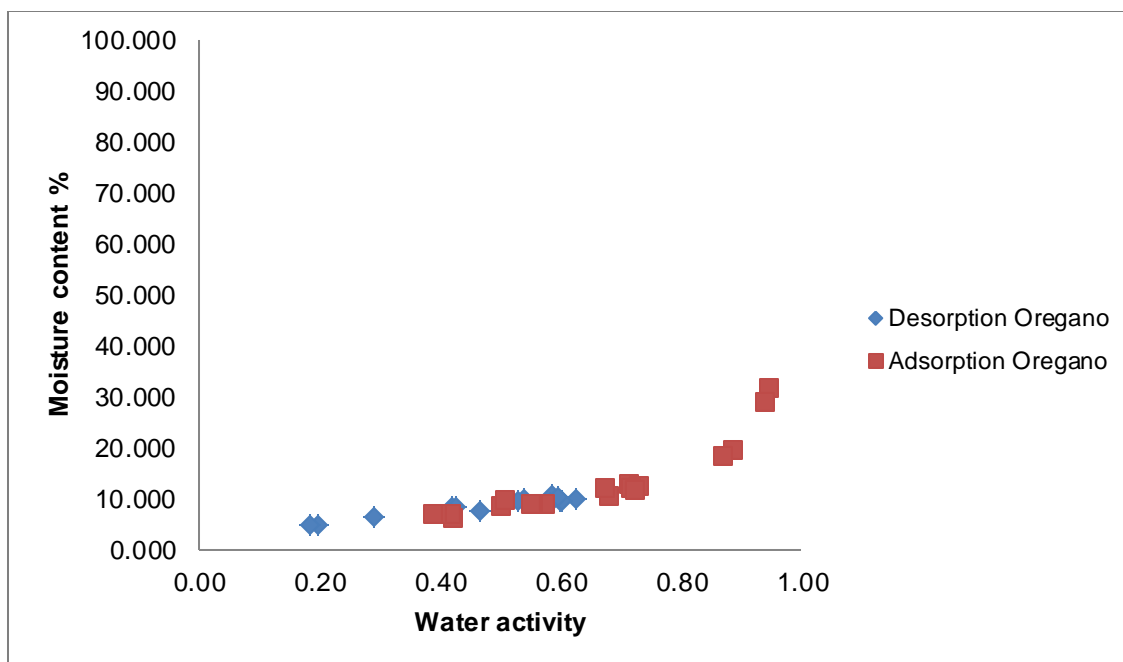


Figure 5.7- Water sorption isotherm for oregano (20°C)

5.3.5 Effect of hygroscopic salt

Salt is an anhydrous substance which becomes deliquescent above a relative humidity of 74% since it begins to sorb large amounts of water vapour (Service, 2002-2013). Salt becomes highly hygroscopic above its critical equilibrium relative humidity of about 75% (Etacude, 2006). Crystalline substances below the critical relative humidity do not undergo changes in their mechanical properties and it is above this point that they start to sorb much water and dissolve (Palzer and Sommer, 2011). In the previous trials, the salt had an $a_w < 0.70$ with very low water content that did not influence the mixing behaviour of the powder mixtures. Hence the salt was stored at relative humidities higher than 70% to identify a relative humidity (RH) that would produce a noticeable increase in moisture content of the salt such that it still retained the solid form and did not form liquid. The salt already began to deliquesce in the range of 73-74% RH. Hence salt at 74%RH was selected and used for mixing with paprika ($a_w = 0.45$) and oregano ($a_w = 0.47$).

Mixing trials were conducted at 50% salt composition (by weight) with both paprika and oregano. During paprika / salt mixing, the mixer couldn't function after the initial 10 seconds of mixing since the powders agglomerated and formed a cake. The salt had sorbed water and become sufficiently cohesive to cake the powder mix. The influence of

water activity on the flow behaviour of salt was determined using the PFT tester and the flow functions are presented in Figure 5.9c. At the lower water activities, the salt is characterised as a very easy flow powder. At $a_w = 0.73$, the flow function changes with a major reduction in powder flowability, and increasing the a_w a little further to 0.75 resulted in another major reduction in the flowability of the salt.

In case of oregano / salt mixture, the mixer could complete the mixing for the 150 s duration and the mixing curve is presented in Figure 5.8. The MQ obtained was much worse than the trials with the higher water content oregano but was similar to the dry oregano and salt, although the reasons for the similarity are not same. Segregation was the reason for the poor MQ for the dry oregano and salt, while the wet salt and oregano produced a very cohesive mix that proved difficult for the paddle mixer to mix.

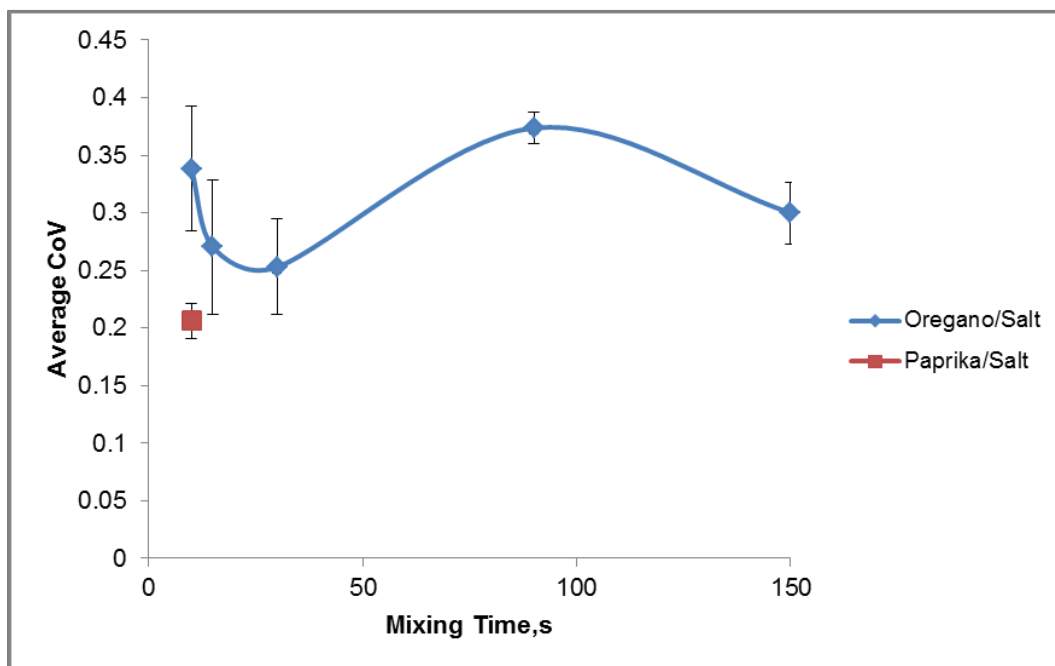
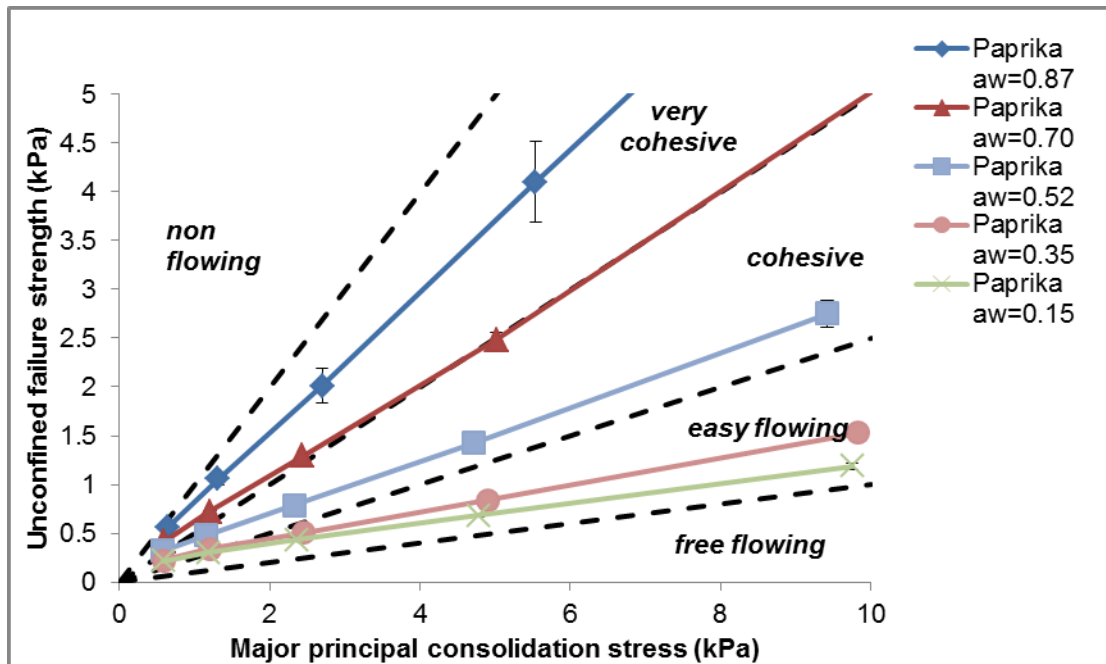
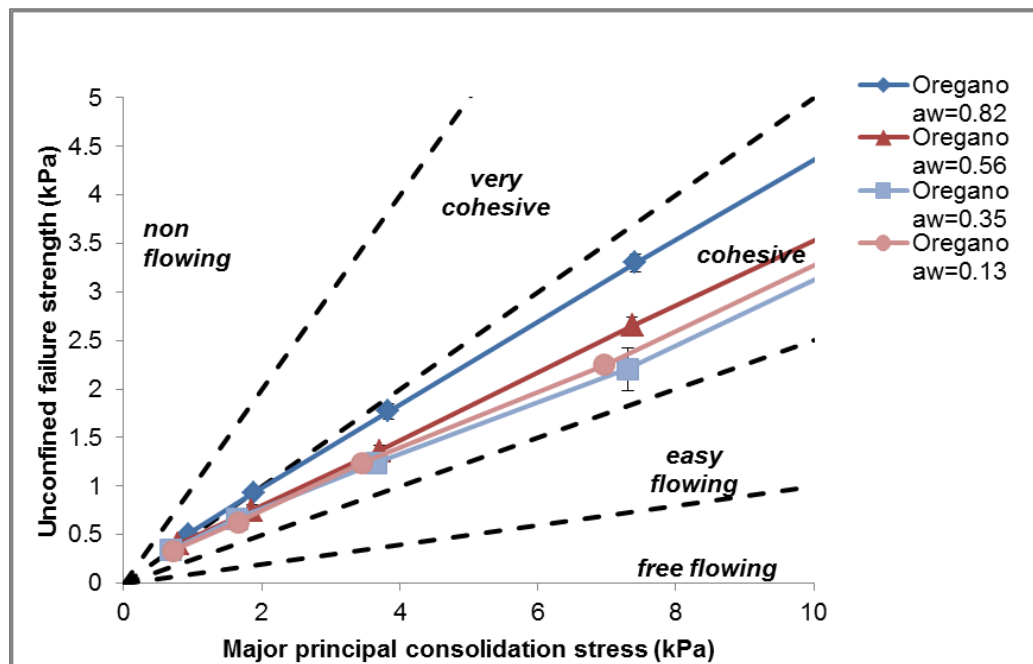


Figure 5.8- Effect of using 74% humidified salt on the mixing of salt with oregano and paprika

(a)



(b)



(c)

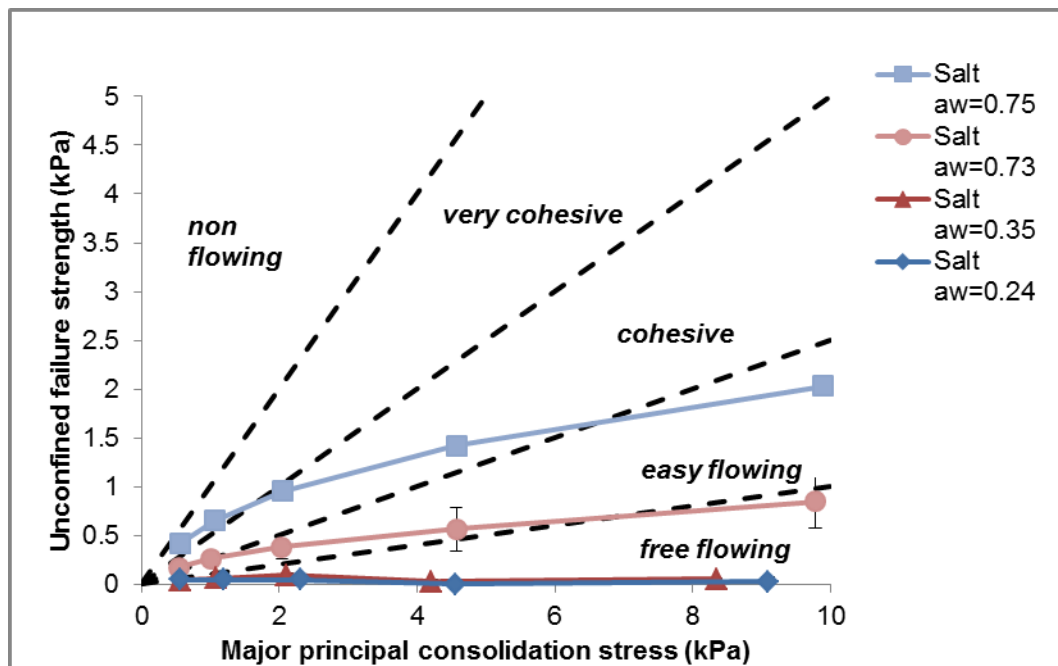


Figure 5.9- (a) Plot showing flow behaviour of paprika for different a_w (b) Plot showing flow behaviour of oregano for different a_w (c) Plot showing flow behaviour of salt for different a_w

5.4 Conclusions

Mixture composition did not affect the mixing characteristics of sugar / salt and paprika / salt mixes in the range of 20 to 80% salt content, however the mixture quality dis-improved at the lower salt concentrations of 1% and less. For oregano / salt, there was a progressive dis-improvement in mixture quality with higher oregano content due to greater void spaces between particles which facilitated salt segregation by sieving. The results showed that composition has a greater influence on the MQ of powders that are more difficult to mix, such as O/S. Increasing the water content of the paprika and oregano, by exposing to high relative humidities, did influence the mixture quality of the mixes, but in different ways. For paprika / salt, the mixing became more difficult and this was most likely due to increased cohesiveness of the paprika at higher water content. On the other hand, the mixture quality of the oregano / salt improved when oregano had higher water content. This is most likely because of the increased cohesion of the oregano whereby the salt particles bound onto and coated the bigger oregano particles which inhibited the segregation tendency of the mix. Although mixture

composition did not affect the MQ of P/S mixture as much as it did for O/S mixture for water activities lower than 50%, when the water content of paprika and oregano were varied, the dependence of MQ was evident for both mixes as a function of the concentration of the individual powders used as well as the water content to form cohesive bonds. Exposing the salt to 74% relative humidity resulted in a large increase in the cohesiveness of the salt due to water sorption, which made it difficult to mix with either the paprika or oregano.

CHAPTER 6

THE STUDY OF EFFECT OF POWDER DENSITIES, PARTICLE SIZE AND SHAPE ON MIXTURE QUALITY OF BINARY FOOD POWDER MIXTURES

Particle size and density are two important parameters which affect the mixture homogeneity of powder mixtures. In this study several types of food powders with different particle size and poured bulk density were chosen for the binary powder mixing trials. In each type of binary mixture salt was one of the main ingredients, hence conductivity analysis was performed on the mixtures and coefficient of variation was used to evaluate the mixture homogeneity. All binary powders were mixed at a ratio 50:50 by weight in a 2L prototype lab-scale paddle mixer. The experiments were conducted in such a way that the ingredients used either had a similar particle size and different bulk density or similar bulk density and different particle size. Different density and size ratios were investigated to observe the limit up to which good mixing takes place. Density differences between the binary powders were varied from 1.5 up to 16.4. The range of size ratio investigated was from 1.96 up to 15.73. Results indicate that powders mixed very well up to a particle size ratio of 4.45. For higher ratios mixture quality disimproved but no segregation was visually observed. The bulk density had a larger influence in affecting the mixture quality (MQ) as compared to particle size. At higher bulk density ratios almost complete segregation was observed and this was majorly influenced by the irregular shapes of thyme and oregano.

6.1 Introduction

Dry powder mixing is widely used across different types of industry and a key aim from the process is to produce a homogenous mixture (Barbosa-Cánovas et al., 2005b; Cooke et al., 1976; Fan et al., 1990; Léonard et al., 2008). It is crucial for the industries to maintain consistent homogeneity in their powder mixture since this helps them to manufacture products with consistent quality, taste, flavour, texture and other properties (Barbosa-Cánovas et al., 2005b, c). Another important step associated with mixing is the assessment of the mixture homogeneity or quality. The attainment and assessment of powder mixture homogeneity is extremely important in pharmaceutical industries to ensure the dosage of the active ingredient is accurate in the dosage unit as costs associated with failure to meet the homogeneity standards are potentially large (Barling et al.; Léonard et al., 2008; Marikh et al., 2008).

Powder mixing is influenced by mixing time, particle size, shape, density and type of powders as well as the design of the mixer used (Barbosa-Cánovas et al., 2005b). Most of the powder mixtures have ingredients with different sizes, shapes, textures and densities (Berk, 2008). Bulk density and porosity are one of the important parameters which help to decide if the raw ingredients used can mix together or not. Barbosa-Cánovas et al (2005a) and Zhou et al (2003) studied the effect of particle density on the mixing performance of similarly sized particles and it was seen that a slight variation in the particle density worsened the performance due to the different forces acting on heavy and light particles. During mixing, different particles can behave differently and the mixtures undergo mixing and demixing in successive stages during this process (Berk, 2008). The physical properties of powders, especially particle size and density play a key role in determining their tendency to segregate or mix properly during and after a mixing operation (Barbosa-Cánovas et al., 2005b; Nienow et al., 1997). If the powders mixed have a similar size, shape and density the tendency to segregate is reduced and they reach a state of equilibrium between the mixing and demixing stages thereby producing the final mix (Barbosa-Cánovas et al., 2005b).

Though differences in density and shape of particles are known to cause segregation in mixtures, often difference in particle size has by far been considered as the most important parameter (Barbosa-Cánovas et al., 2005b; Tang and Puri, 2007; Williams, 1976). The particle size distribution of the ingredients used in a powder mixture is one

of the key factors that determine the homogeneity of the mixture (Chowhan, 1979; Devriendt et al., 2013). When the size difference between particles is larger the difficulty to mix the particles also increases (Zhou et al., 2003). Small particles show a tendency to fall downwards leading to segregation (Axe, 1995; Graversen, 2012). A study by Drahun and Bridgwater (1983) suggests that particle density ratio influences segregation and that free surface segregation can be minimised by maintaining an appropriate balance between the size and density ratios. Particle size distribution also affects other powder properties such as bulk density, flowability and compressibility (Barbosa-Canovas et al., 1987; Peleg, 1977). Barbosa-Canovas et al (1985) reported that differences in particle size can cause segregation in a free flowing powder mixture. As the particle size decreases for a given powder, the degree of contact area between the particles increases thereby strengthening the intermolecular forces and reducing the ease of flow of the powder which can reduce segregation tendency (Landillon, 2008). In this study, physical properties, such as particle size and shape, bulk density and particle density were measured for different types of food powders that are used in the commercial manufacture of spice mixtures. Since differences in these properties are key parameters which affect mixing homogeneity, the objective of this study was to investigate the influence of differences in these properties on the mixing behaviour of binary food powder mixtures. Two sets of mixing trials were undertaken, one where powder densities were varied and another where particle size was varied. Images of particle shape of the powders were taken to investigate its influence.

6.2 Materials and Methods

6.2.1 Powders used for mixing and powder property measurement

Several different food powders including dried herbs, sugars and salts of different shapes and sizes that are commonly used in the manufacture of different flavour seasonings were procured from Santa Maria AB, Sweden (Figure 6.1). The particle size and densities of the powders were measured (Powder property data given in chapter 3). These data were used to select 12 powders that had suitable property values for this study. Five of the powders were different sized salts. The selected 12 powders along with their particle size and densities are presented in Table 6.1.

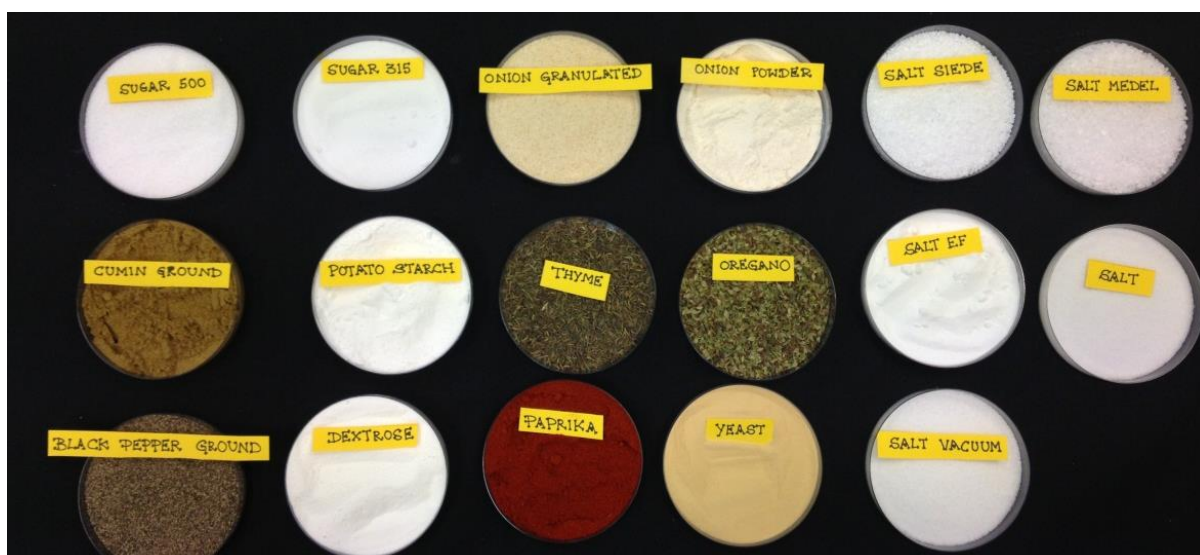


Figure 6.1- Powders used for screening

Table 6.1- List of selected powder and their property data (Average values from six repeat trials)

No.s	Name of powder	Bulk Densities		Particle Density (kg/L)	Particle Size (µm)		
		Poured density (kg/L)	Tapped Density (kg/L)				
1	Salt	1.283	1.403	2.165	231	436	718
2	Salt EF	1.267	1.434	2.158	32	110	253
3	Salt Vacuum (Salt V)	1.182	1.262	2.155	367	692	1185
4	Salt Medel (Salt M)	1.085	1.151	2.132	1250	1460	1600
5	Salt Siede (Salt	1.061	1.141	2.134	538	993	1572

	S)						
6	Sugar 500	0.857	0.947	1.589	236	542	1022
7	Potato starch	0.699	0.783	1.447	24	44	75
8	Onion Granules	0.649	0.702	1.510	185	364	626
9	Paprika	0.454	0.517	1.364	67	223	485
10	Blackpepper	0.371	0.438	1.343	72	345	706
11	Thyme	0.176	0.212	1.270	437	863	1488
12	Oregano	0.066	0.073	1.208	1250	1600	-

6.2.2 Mixing and Sampling

The powders shown in Table 6.2 were selected for the binary mixing trials. The two powders in all binary mixes were mixed in equal proportions by weight (50:50). The powders were placed side by side inside the mixer to start from a fully segregated medium. The mixing was carried out for up to 150 s and samples were withdrawn from predefined specific points across the mixer at fixed time intervals of 10s, 15s, 30s, 90s and 150s (for detailed information refer chapter 4).

Table 6.2- Powders used in the binary mixes for the density ratio and size ratio trials

No.	Density ratio trials	No.	Size ratio trails
D1	Sugar500 – Salt	S1	Paprika – Salt
D2	Onion granules - Salt	S2	Paprika – SaltEF
D3	Blackpepper - Salt	S3	Potatostarch – SaltEF
D4	Thyme – Salt Se	S4	Paprika – Salt V
D5	Thyme – Salt V	S5	Paprika – Salt S
D6	Oregano – Salt S	S6	Paprika – Salt M
D7	Oregano – Salt M	S7	Potatostarch - Salt
		S8	Potatostarch – Salt V

6.3 Results and Discussion

6.3.1 Effect of differences in powder densities

To investigate the influence of differences in powder densities (bulk and particle) on the mixing of the powders, trials were conducted with 7 binary mixes containing powders with similar sizes but different densities, as presented in Table 6.2 and Table 6.3. The size ratios (higher / lower) were less than 1.3, except for D6 at 1.61. There was a large variation in the poured bulk density ratios ranging from 1.5 to 16.4, while the particle density ratios had much less variation, ranging from 1.36 to 1.77.

Table 6.3 shows the influence of differences in densities between the two components (or density ratios) on the mixture quality (MQ) at the end of mixing, as represented by the CoV at 150 s. The difference in bulk density (bulk density ratio) has a strong influence on the mixture quality. For the lower bulk density ratios, less than 3.5 (D1, D2, D3 in Table 6.3), very good mixture quality was achieved as CoV is a lot less than 0.06. However, for the higher ratios, > 6.2 (D4 to D7), unsatisfactory mixture quality was achieved as the CoV values were well above 0.06 and the mixes were visually

segregated at the end of mixing. These results show that differences in bulk density may have an impact on mixture quality, especially when the bulk density ratio exceeds a value somewhere in the range from 3.5 to 6.

Table 6.3- Influence of density ratios for binary mixtures on the CoV values at the end of 150s of mixing (Trial No. – refer to Table 6.2)

Trial No.	Ratios (higher / lower)			Average Size (μm)	Porosity² (%)	CoV at 150s
	Bulk Density¹	Particle Density	Size D₅₀			
D1	1.50	1.36	1.24	489	46	0.02
D2	1.98	1.43	1.20	400	57	0.01
D3	3.46	1.61	1.26	391	72	0.02
D4	6.03	1.68	1.15	928	86	0.13 ± 0.02
D5	6.72	1.70	1.25	778	86	0.14 ± 0.01
D6	16.08	1.77	1.61	1297	95	0.14 ± 0.06
D7	16.44	1.76	1.10	1530	95	0.21 ± 0.05

¹ Poured bulk density.

² Porosity of powder with lowest bulk density in the binary mix.

Differences in particle density may induce a segregation mechanism that reduces MQ, where the denser particles move downwards and the less dense particles move upwards. In this study, there were significant differences in particle density, with particle density ratios ranging from 1.36 to 1.77. Table 6.3 suggests that there is a possible link between differences in particle densities and mixture quality. However, the variation in particle density ratios was much lower than that for bulk density ratios and therefore it is believed that the differences in bulk density are having a more significant

influence. The porosity of the lower bulk density component in each binary mix (i.e. the non-salt component) was calculated using equation 3 and is also presented in Table 6.3.

$$\%Porosity = 100 \left(1 - \frac{\rho_B}{\rho_P} \right) \quad (3)$$

where:

ρ_B poured bulk density

ρ_P particle density

The porosity data shows that the lower bulk density powders used in trials D4 to D7 have very large porosity and there is very large voidage between the particles. This would suggest that the poor mixing in these trials was due to segregation based on the denser salt particles sieving downwards through the large void spaces that exist between the less dense particles. The large voidage is most likely due to the irregular shapes of the thyme and oregano used in these four trials, and this is discussed in more detail in section i.

Table 6.3 also presents the average particle size in each mix and shows a trend with mixture quality. Thus, it could be argued that there is also a relationship between average particle size and mixture quality, however it is believed that this is not as significant a factor as difference in bulk density, although particle size may influence the size of individual voids and how the salt particle sieves through these voids.

Table 6.3 provides CoV data at the end of mixing only. Figure 6.2, Figure 6.3 and Figure 6.4 provide the mixing curves for the trials, where they show and compare the mixture quality over the duration of mixing. It can be seen from Figure 6.2 that for the mixtures sugar500 - salt (D1) and oniongranules - salt (D2), which have a bulk density ratio of 1.49 and 1.97 respectively, very good mixing takes place within the first 30 seconds and the CoV remains very low until the end of mixing. For blackpepper - salt (D3), although the density ratio is higher than these two mixtures, it still reached a good degree of mixing after 30 s of mixing inside the paddle mixer. Therefore for bulk density ratios up to 3.46 very good degree of mixing and mixture quality is obtained as CoV was 0.01 or 0.02 for these mixtures. In industries during process development CoV values of 1% or

2% are preferred in order to reduce the homogeneity loss during scale-up of the process (Berthiaux et al., 2008).

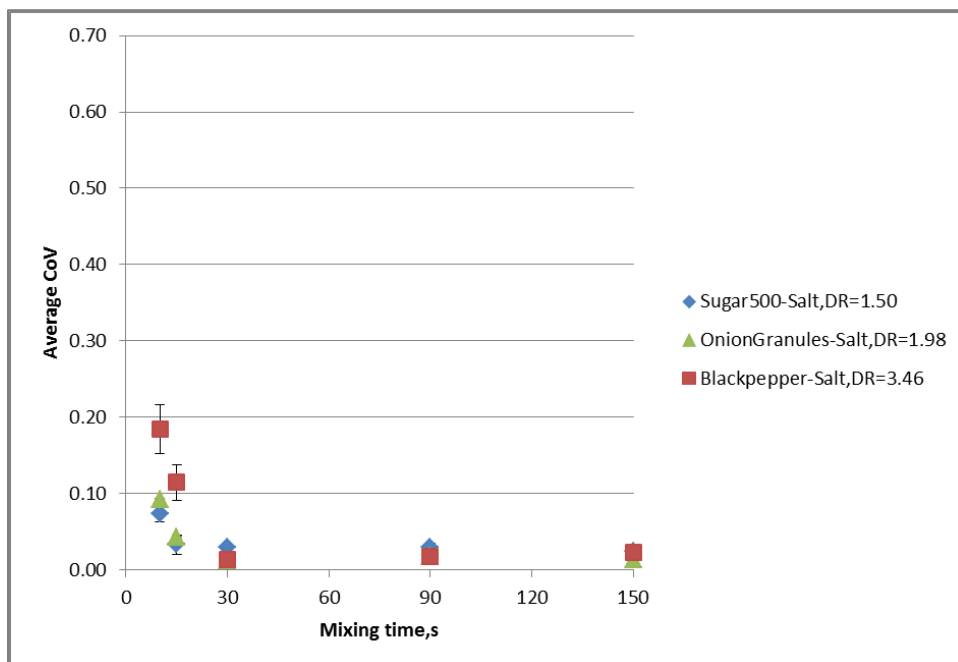


Figure 6.2- Effect of poured bulk density ratio (DR) - Mixing curves for Sugar500 - Salt mixture; Oniongranules - Salt mixture; and Blackpepper - Salt mixture

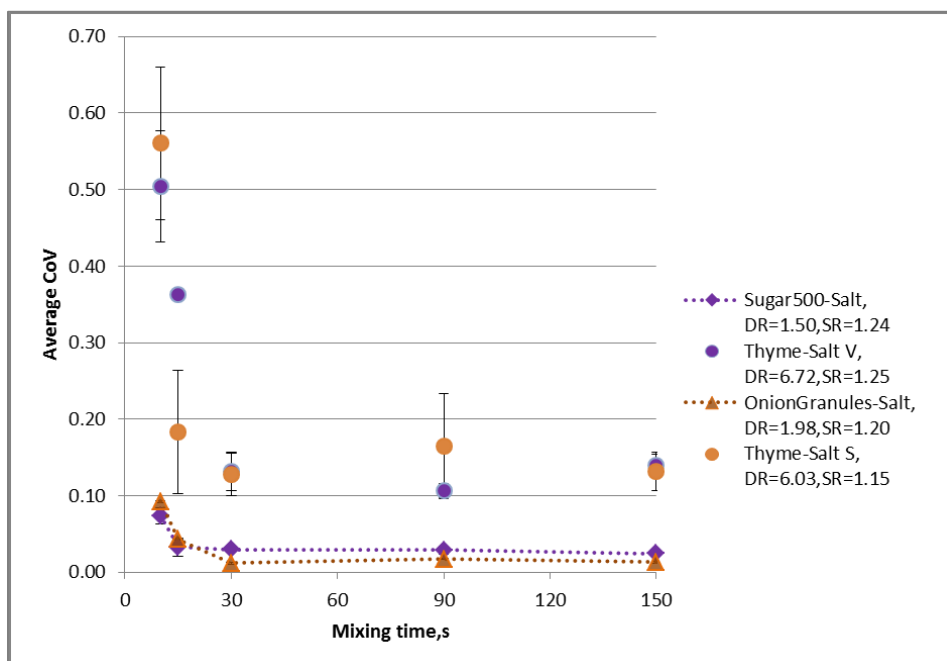


Figure 6.3- Effect of poured bulk density ratio (DR) - Mixing curves for trials with size ratios of 1.25 and 1.2

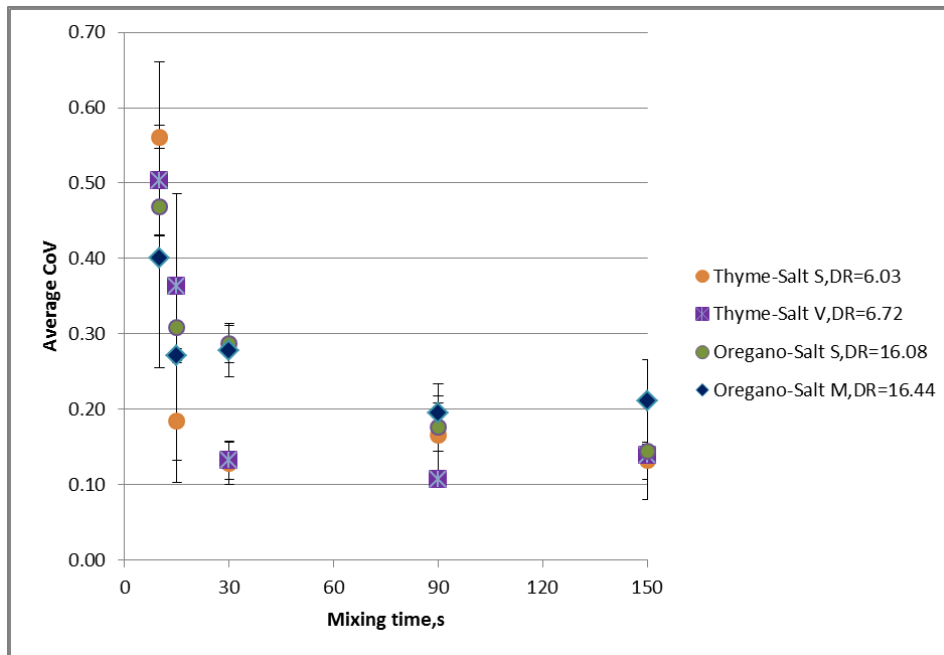


Figure 6.4- Effect of poured bulk density ratio (DR) - Mixing curves for Thyme – Salt S mixture; Thyme - Salt V mixture; Oregano - Salt S mixture; and Oregano – Salt M mixture

Figure 6.3 compares the mixing of sugar500 - salt mixture (D1) with thyme - saltvacuum mixture (D5), which has a very similar size ratio of about 1.25 and also the oniongranules - salt mixture (D2) with the thyme - saltsiede mixture (D4), which also have similar size ratio of 1.2. It can be seen that at much higher bulk density ratios there is a significant effect on the MQ of the binary powder mixtures. For the oniongranules - salt mixture and sugar500 - salt mixture the CoV is below 0.06 within the first 30s of mixing whereas for the thyme - saltsiede mixture and thyme - saltvacuum mixture with bulk density ratios of 6.03 and 6.72 respectively the CoV is 0.13 and 0.14 even after 150s mixing time. Therefore, it is observed that even if the powders mixed in two different binary powder mixtures have the same size ratio between their ingredients if the bulk densities vary by a large margin for the ingredients used in the mixtures, the mixing behaviour is highly affected. This is contrary to what is reported by Williams (1976) which mentions that differences in particle size are the main cause for segregation in powders.

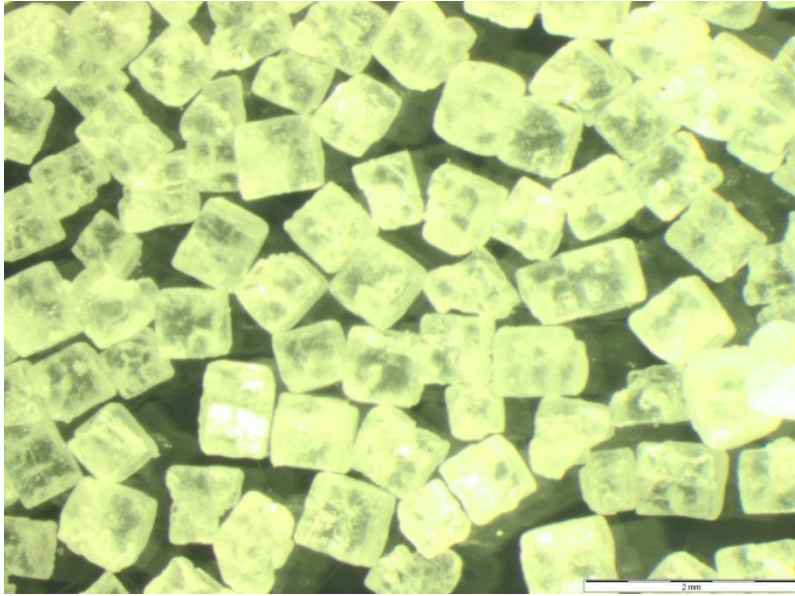
During mixing and handling of particles which have large differences between their densities they can undergo segregation, as the lighter particles flo at upwards and the

dense particles move downward (Axe, 1995; Graversen, 2012). Trials performed using oregano - salt sieved (D6) and oregano - salt medel (D7) showed similar segregation tendencies and the ability to mix was very poor, as illustrated in Figure 6.4 by the poor mixture quality achieved over the entire mixing time.

i. Effect of particle shape

Particulate matter and powders can have different types of shapes especially when they are organic in nature. The shapes can vary from being needle-like and plate-like to globular and spherical (Barbosa-Cánovas et al., 2005c). Images of the shapes of salt, oregano and thyme are presented in Figure 6.5. The salt has a more regular block type shape, while the oregano and thyme have more irregular shapes. The oregano has a leafy type shape and thyme has a needle type shape. Most of the other powders tested had regular block or globular shapes. The black pepper and onion granules have particles that have similar shape as that of the salt particles and Table 6.1 shows that their particle size distribution is similar to that of salt and their median particle size is also similar. Both black pepper and onion granules have fine particles that are smaller than D10 salt particles ($231\mu\text{m}$). This helps to group similar sized particles together and promotes coating of the fines on the larger sized particles thereby improving the MQ (Figure 6.5e and f). It is believed that the shapes of the oregano and thyme resulted in the high voidage which produced the very low bulk densities for these powders. This ultimately caused the segregation mechanism which produced the poor mixing with the salts, as illustrated for thyme-salt vacuum in Figure 6.5d. Axe (1995) and Swaminathan and Kildsig (2002) described that when the shape of particles in a mixture is extremely different from each other it can lead to segregation and the particles can also have hindered flowability and packing ability. The presence of irregularly shaped and coarse particles increases the chances of segregation potential (Tang and Puri, 2007).

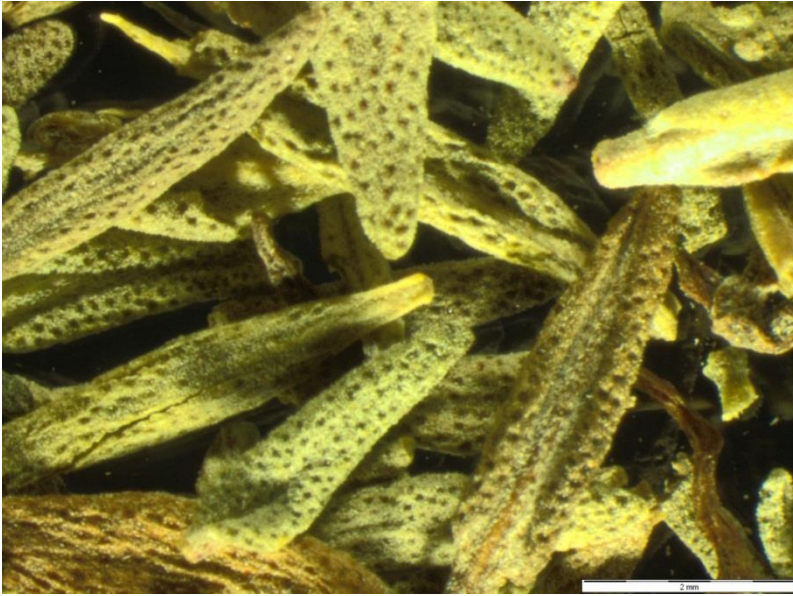
(a)



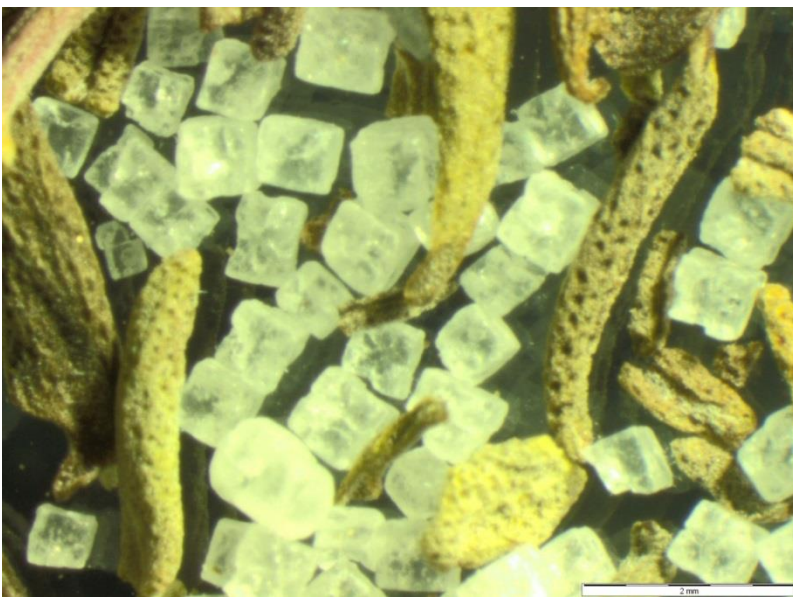
(b)



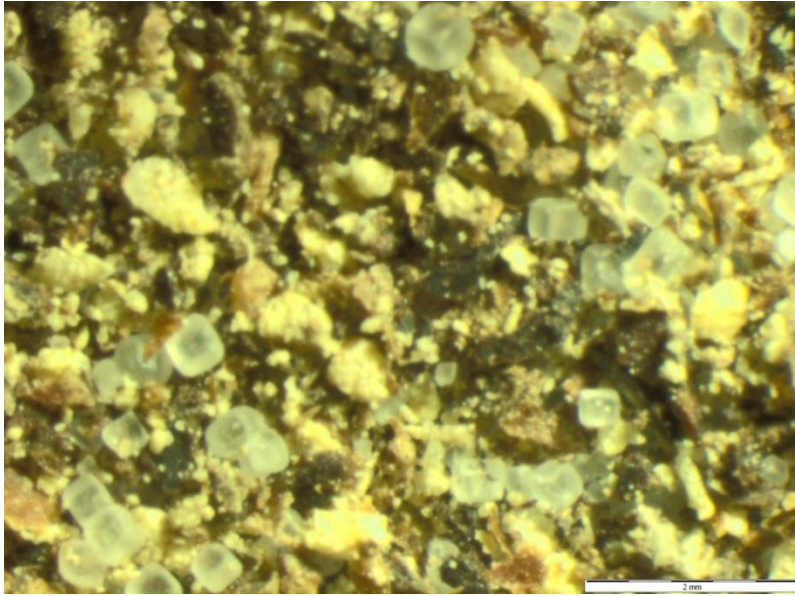
(c)



(d)



(e)



(f)



Figure 6.5- Images of a) Salt V; b) Oregano; c) Thyme; d) Thyme and Salt V; e) Black pepper and Salt; f) Onion Granules-Salt

ii. Effect of differences in particle size

To investigate the effect of particle size on the MQ of binary powder mixtures, trials were performed using paprika and potato starch with salts of different particle sizes in

which the density difference between the two ingredients for each type of binary mixture was almost similar. Ideally, in trials like these, it is desirable to have powders with identical densities, however salt is used in all trials and it is much denser than all of the other powders. Thus, 8 trials were selected such that the bulk density ratios of the component powders were similar. Five of the trials were paprika with different size salts. From Table 6.4, it can be seen that the bulk density ratios of all the paprika-salt mixtures is between 2.34 – 2.83 and only the size ratio varies widely for these mixtures. The size ratios ranged from 1.96 up to 6.55. Three of the eight trials were potato starch with different size salts. The bulk density ratios were similar ranging from 1.69 to 1.84 and the size ratio ranged from 2.50 to 15.73. The bulk density ratios were well within the range of ratios that achieved good mixing in section 3.1. The particle density ratios were all very similar in the range of 1.49 to 1.59.

Table 6.4- Influence of size ratio for binary mixtures on the CoV values at the end of 150s of mixing (Trial No. – refer to Table 6.2)

Trail No.	Ratios (salt / non-salt)			Ave.	CoV at 150s
	Size D₅₀	Bulk Density¹	Particle Density	Size (μm)	
S1	1.96	2.83	1.59	330	0.06 \pm 0.01
S2	2.03	2.79	1.58	167	0.02
S3	2.50	1.81	1.49	77	0.02
S4	3.10	2.60	1.58	458	0.03 \pm 0.01
S5	4.45	2.34	1.56	608	0.03
S6	6.55	2.39	1.56	842	0.06 \pm 0.01
S7	9.91	1.84	1.50	240	0.06 \pm 0.01
S8	15.73	1.69	1.49	368	0.08 \pm 0.04

¹ Poured bulk density.

The influence of size ratio on MQ for all 8 trials is presented in Table 6.4. For the first 5 trials (S1 to S5), where the size ratio is less than 4.5, very good MQ was achieved, as illustrated in Figure 6.6a for paprika-SaltEF, with CoV values of 0.03 or less (S1 has a CoV of 0.06 but this is believed to be an outlier value or a result of overmixing as explained later. In chapter 5 it is seen that this mixture has a CoV of 0.05 which is still below the 6% upper limit and is considered as a good mixture). As the size ratio increased in trials S6 to S8, MQ disimproved to 0.06 and 0.08. However, even at the very large size ratio of nearly 16 the CoV of 0.08 was not too much outside the satisfactory upper limit CoV of 0.06, and was much better than the poor density ratio trials (D4 – D7). Overall, Table 6.4 shows that difference in particle size can influence MQ. Very good MQ was achieved at size ratios below 4.5. At higher size ratios the influence is not as large as might have been expected, particularly at the size ratio of nearly 16. One of the effects that may occur at high size ratios is small powder particles may coat large

particles due to cohesive attractions and the large specific surface area of the small particles (Pasha et al., 2014). This can be seen in Figure 6.6b for paprika – saltmedel (size ratio = 6.55), where the small paprika particles are coating the large salt particles. This effect may help in counteracting a segregation tendency due to large differences in particle size.

(a)



(b)

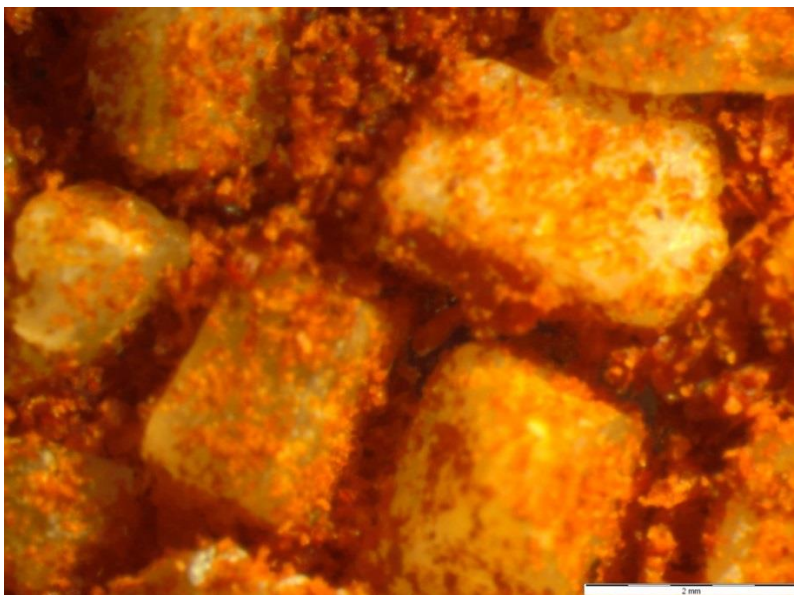


Figure 6.6- Images of a) Paprika – Salt EF (size ratio = 2.03); and b) Paprika – Salt M (size ratio = 6.55)

Figure 6.7 and Figure 6.8 show the mixing curves for the paprika – salt and potato starch – salt trials, respectively. From Figure 6.7 it can be seen that for paprika - salt mixtures, the CoV is below 0.06 for most of the binary mixtures studied except for paprika - salt (S1) where the CoV is 0.06. Looking at the mixing curve for S1 in more detail shows that it's CoV actually decreased quite rapidly to 0.03 after 30 s and remained at 0.03 at 90 s. Consequently, it is believed that the increase to 0.06 at 150 s is either an outlier value due to the random nature of mixing or as a result of overmixing (Fitzpatrick, 2009) and that a CoV of 0.03 can be achieved and is a more representative value. In the case of potato starch mixed with different types of salt (Figure 6.8), all these 3 mixes mixed very rapidly with CoVs being near their final values after only 10 s of mixing. For the highest size ratio (S8), the MQ at all reported times is better than at the end, being less than or equal to 0.06, which suggests that satisfactory MQ can be achieved at a size ratio of 16. Visual inspection of the mix showed that the powders seemed to mix well.

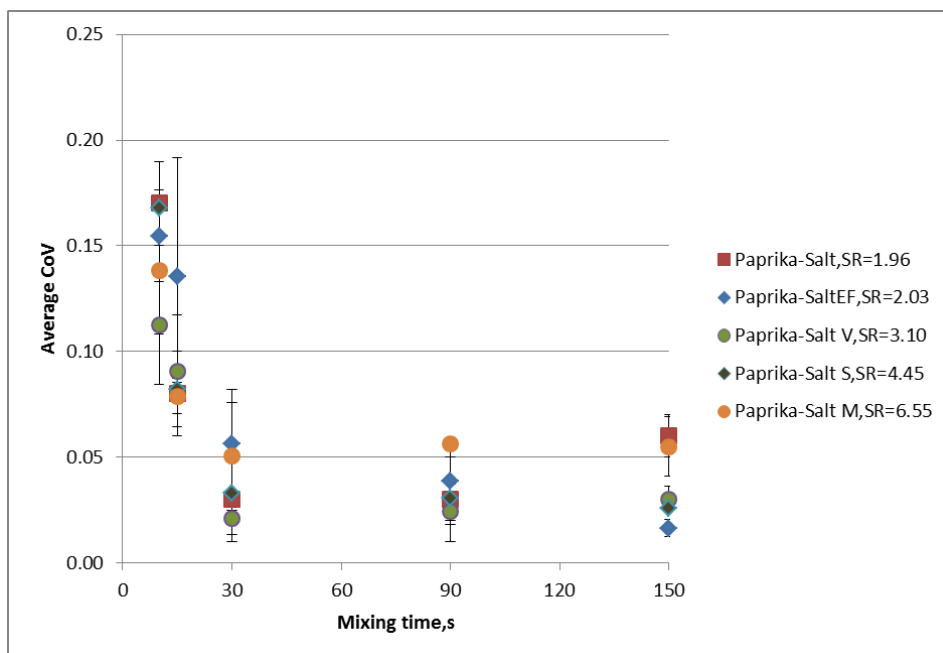


Figure 6.7- Effect of particle size ratio (SR) - Mixing curves for Paprika mixed with a) Salt; b) Salt EF; c) Salt V; d) Salt S; and e) Salt M

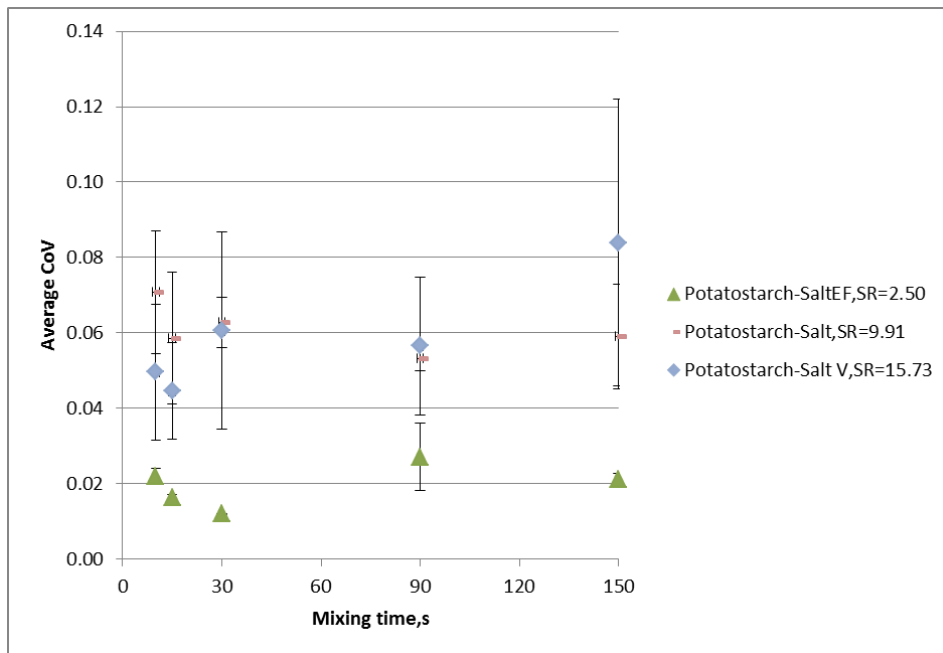


Figure 6.8- Effect of particle size ratio (SR) - Mixing curves for Potato Starch mixed with a) Salt EF; b) Salt; and c) Salt V

For the paprika and potato starch powders mixed with salt extra fine (S2 and S3), both mixes had very good mixing with the lowest CoV values of 0.02. This is most likely due to the smaller particle sizes, especially the salt EF and potato starch, which caused increased interaction between the powder particles due to larger contact area and this enabled very good uniformity to be achieved (Kuakpetoon et al., 2001).

6.4 Conclusions

Difference in bulk density between the salt and food powders displayed a very big influence on the mixture quality (MQ) of the binary mixes. Very good MQ was achieved for bulk density ratios less than 3.5. However, poor MQ with visually observed segregation was obtained for mixes with bulk density ratios greater than 6. This was most likely due to the low bulk densities of the non-salt powders, that is, thyme and oregano, although particle size and differences in particle density may also be contributing. The low bulk density of these powders was not due to unusually low particle densities, but due to unusually large porosity or voidage between the particles, which was mostly likely caused by the irregular shapes of the thyme and oregano. Consequently, differences in particle shape can influence MQ. The large voidage allowed

the more regularly shaped salt particles to move downwards through the voids and this created a strong segregation mechanism that counteracted the mixing mechanism in the paddle mixer.

Differences in particle size had an effect on MQ but it was not as large as initially expected. Size ratios above somewhere in the region of 5 led to poorer MQ but these were just at the limit of satisfactory MQ with a CoV of 0.06, even for the extreme size ratio of nearly 16. This may in-part be due to finer particles coating the larger particles due to their cohesiveness, thus counteracting the size segregation tendency. Overall, in this study, the differences in bulk density and shape had a much stronger influence on MQ than differences in particle size and particle density. Of course, dry powder mixing is a complex operation and there are many factors that come together to determine the MQ of a mix, including mixer type and operation conditions along with the many powder properties highlighted in this study such as bulk and particle densities, particle size and shape and cohesiveness.

CHAPTER 7

EVALUATION OF A DIGITAL COLOUR IMAGING SYSTEM FOR ASSESSING THE MIXTURE QUALITY OF SPICE POWDER MIXES BY COMPARISON WITH A SALT CONDUCTIVITY METHOD

Mixture quality or homogeneity analysis is a crucial step in powder industries to evaluate if the final product meets the requisite standards and therefore industries prefer a method that is reliable and easy to use. In this study the mixture quality of food powder mixtures that differ in mixability and number of components is studied by using digital colour imaging method (DCI) and comparing it with a salt conductivity method. Two binary food and two quaternary food powder mixtures with different coloured particles were studied. Salt was one of the key ingredients commonly used in all the mixtures. The digital colour imaging method was used to measure colour of the different mixtures and by using conductivity analysis the concentration of salt in each mixture was studied and coefficient of variation (CoV) was used to determine the homogeneity of the mixture. Results showed that both methods gave similar results for the well mixing paprika-salt mixture however the DCI method did not work for the oregano-salt mixture which was highly segregating in nature. When the colour difference between the powders was high the DCI method showed a good trend with the salt concentration method. When quaternary mixture consisting of similar coloured particles and segregating particles was used this trend was weaker as compared to the mixture that consisted of cohesive powders that mixed well with each other although they had some particles that were similarly coloured. Overall it showed that DCI method has a potential for use by industries that can analyse powder mixtures with components that have differences in colour and that are not segregating in nature.

7.1 Introduction

Mixing of powders and dry particulates is a commonly used industrial operation and the basic principles can be applied to food powders (Fitzpatrick, 2009; Sommer, 2000).

Particulate mixtures, such as flavour seasonings, cereal mixes, cake mixes and soups mixes, which include ingredients that are either in powder or particulate form such as flour, nuts, dried vegetables and fruits and dairy powders, are commonly manufactured in the food industry (Fitzpatrick, 2009). Powdered foods can be sold as ingredients, semi-finished or finished products (Carillo et al., 2012) and the dry nature of the products makes them easy to store, transport and improves product shelf life (Fitzpatrick and Ahrne, 2005). As the demand for ready to use powdered products is increasing, industries are constantly in search of techniques that are faster, economical, reliable and easily adoptable to use for product quality analysis. In the case of powder mixtures the quality of the final product is determined by evaluating the powder mixture quality or homogeneity.

Powder mixture homogeneity is an extremely important parameter that determines the quality, performance, the functional and the end use of the product. It is a crucial parameter in the pharmaceutical where the demands to meet the specified standards are very high (Bellon et al., 2013; Hamad et al., 2010; Huang and Kuo, 2014; Portillo et al., 2009). Traditional techniques for assessing mixture quality require sampling across different regions of the powder bed and measuring the concentration of a specific component in each sample, such as salt. One such commonly used sampling technique involves the use of a thief probe sampler that has to be inserted inside the powder bed to extract representative samples from the bed (Cooke et al., 1976; Muzzio et al., 2003). This method has some drawbacks such as it can give a biased estimation of the powder uniformity as it depends on the skills of the operator who does the sampling and analysis and therefore is susceptible to sampling and analytical errors (Muzzio et al., 1997). Thief sampling disturbs the original state of the powder mixture and powders being dynamic in nature the desired mixedness can be easily disrupted when any external force such as vibration or shaking is applied (Barbosa-Cánovas et al., 2005b; Bridgwater, 2012). Thus there is a need to use techniques which can assess mixture quality more easily and in a non-destructive fashion (Muzzio et al., 2003).

The demand and focus towards novel, quicker and easily adoptable methods to evaluate mixture quality of powder products has been increasing rapidly. Image-analysis (Aissa et al., 2010b; Boschetto and Giordano, 2012; Rosas and Blanco, 2012), capturing video of the mixing process to analyse the process step by step (Cabaret et al., 2007), Near Infra-Red Spectroscopy (He et al., 2013; Kehlenbeck, 2011) and laser-induced fluorescence (LID) (Lai et al., 2001) are some of the alternative approaches to measure mixture uniformity which are non-invasive in nature. Image analysis has become a growing trend and taking photos at the mixture surface to determine the composition is one of the easiest ways to record the distribution of powders on the bed or inside the mixer (Berthiaux, 2006; Huang and Kuo, 2014; Le Coent, 2005). However it requires treatment of images with relevant software to correct the background lighting or to enhance the pixels in the image (Le Coent, 2005; Muerza, 2002).

Although the traditional technique has its limitations in terms of sampling and analysis as mentioned above, it is still the preferred method to do mixture quality analysis in most of the industries. Since powders are stored in silos or big bags, thief probes are used to take samples from across different cross sections in the bag and the concentration of one of the components (which can be the tracer component) is determined to estimate the mixture quality or homogeneity and based on the application of the final product the sample is analysed accordingly. For example, if it were an infant milk formula a test could be done to check the amount of vitamins in the milk and in case of a savoury spice mixture one could estimate the concentration of salt.

The work presented in this paper is a continuation of work from chapter 4 in which a Digital Colour Imaging (DCI) method was used and it was seen that it has potential to assess the mixture quality of binary powder mixtures which have significant differences in the colour of the ingredients. The objective of the current study was to further investigate the potential of the DCI method for assessing mixture quality of spice powders by comparing it with a salt conductivity method. Sampling and measurement of a specific chemical component, such as salt concentration, is a commonly used approach to assessing mixture quality of powder mixes and salt is commonly used in food powder mixes, including spice mixes. Four different spice mixtures (two binary and two quaternary mixtures) were produced in a lab-scale paddle mixer, where salt was one of the components in each mix. In the binary mixes, there was a big colour

difference between the powders, however one mixture mixed very well and the other very poorly. Likewise, for the quaternary mixes, there were good and poor mixes, however each mix had two components with very similar colours that could potentially be difficult for the DCI method to distinguish.

For both the DCI method and salt conductivity method, a number of samples were taken and the mixture quality was assessed by the DCI method first and then by salt conductivity. The advantages of the DCI method over the salt conductivity method includes greater convenience where the measurement is easier to perform as it simply involves placing samples in a controlled optical chamber and taking an image. Visual assessment by operators or lab technicians is often undertaken in the food industry to assess mixture quality. The DCI method offers an advantage in terms of providing an objective visual assessment, which is independent of one persons' subjective assessment. Furthermore, the DCI method does not rely on the measurement of one specific component but instead measures the colour of the whole sample. The method does rely on having sufficient differences in colour between component particulates, and the method will not work if sufficient colour differences are not present. In spice formulations, component powders come in a variety of different colours, thus this was a motivation for investigating the application of the DCI method to spice mixes.

7.2 Materials and Methods

7.2.1 Powder Mixtures

Four different types of powder mixtures were prepared using food powders that are commonly used in different seasonings. The different mixtures prepared are presented in Table 7.1. The powders were procured from Santa Maria AB, Sweden. The two binary powder mixtures used in this study have significant differences in mixability. As seen in chapter 5 the paprika-salt mixture produces a good mix while the oregano-salt mixture produces a segregating mix. The oregano has a very low bulk density and large voidage which allows the salt particles to sieve through the voids producing a segregating mix. The quaternary mixtures were formulated such that one is better mixing in nature compared to the other. One quaternary mix consisted of onion powder and black pepper in addition to paprika and salt which were considered as well mixing powders

due to their similar bulk densities Table 7.2. In the other quaternary mix, the onion was replaced by oregano and this resulted in a mix that had a segregation tendency.

Table 7.1-Different types of powder mixtures used

Name of Mixture	Type of Powder Mixture	Powder 1		Powder 2		Powder 3		Powder 4	
		Name	(%) w:w	Name	(%) w:w	Name	(%) w:w	Name	(%) w:w
Paprika: Salt (P/S)	Binary	Paprika	50	Salt	50	-	-	-	-
Oregano :Salt (O/S)	Binary	Oregano	50	Salt	50	-	-	-	-
Good Mix (GM)	Quaternary	Paprika	30	Salt	20	Onion Powder	30	Black Pepper	20
Poor Mix (PM)	Quaternary	Oregano	30	Salt	20	Paprika	30	Black Pepper	20

Table 7.2-Median particle size and poured bulk density for the individual powders used

Name of Powder	Median particle size d(0.5) (µm)	Poured Bulk Density (kg/L)
Paprika	223	0.454
Oregano	1600	0.066
Black Pepper	345	0.371
Onion powder	40	0.548
Salt	436	1.283

7.2.2 Mixing and Sampling

The component powders in all four mixes were initially placed adjacent to each other to represent a fully segregated medium inside the 2L prototype paddle mixer, which was made of plexiglass. Specific sampling points were selected from throughout the mixing region. A total of nine samples were withdrawn using a bent spoon that resembles a thief probe sampling technique at five different mixing times. The mixing times selected for this study were 2s, 5s, 10s, 30s and 150s. The withdrawn samples were directly placed in small cups with a diameter of 4cm and height of 1cm. The colour of each sample was measured using the DCI method and then the salt concentration of each sample was measured using the salt conductivity method, which are described in the following sections.

7.2.3 Determination of Mixture Quality using DCI Method

The digital colour imaging system DigiEye was used to measure the colour of the samples withdrawn during the experiments. Each sample was placed inside the DigiEye chamber and the DigiEye camera took an image of the mixture. The CIELAB colour coordinates L^* , a^* and b^* were measured and ΔE (the colour value relative to white space) was calculated from equation 1.

$$\Delta E = \sqrt{(L^* - L^*_{standard})^2 + (a^* - a^*_{standard})^2 + (b^* - b^*_{standard})^2} \quad (1)$$

where $L^*_{standard}$, $a^*_{standard}$ and $b^*_{standard}$ are the values measured for white space.

The sample variance in ΔE (Variance ΔE) was calculated from equation 2 and coefficient of variation ($CoV_{\Delta E}$) was calculated from equation 3, and this was used as a measure of mixture quality of the powder mix using the DCI method.

$$Variance \Delta E = \frac{\sum_{i=1}^N (\Delta E_i - \Delta E_{ave})^2}{9} \quad (2)$$

where:

ΔE_i is the ΔE in sample i

ΔE_{ave} is the average ΔE for the 9 samples.

$$CoV_{\Delta E} = \frac{\text{Variance } \Delta E}{\beta} \quad (3)$$

where β is the average ΔE at the respective mixing time (150 s)

7.2.4 Determination of Mixture Quality using Salt Conductivity Method

The same samples were then used for conductivity analysis by diluting them to a specific concentration using deionised water. From the conductivity measurements of the samples, the salt concentration in each of the samples was evaluated by using the calibration curve (as mentioned in Chapter 3). The sample variance (S^2) was then evaluated by inserting these data into equation 4. The mixture quality using the salt conductivity method was assessed by evaluation of the coefficient of variation (CoV) in equation 5.

$$S^2 = \frac{\sum_{i=1}^9 (C_i - C_{\text{average}})^2}{9} \quad (4)$$

where:

C_i salt concentration in sample i

C_{average} average concentration of salt

$$CoV = \frac{S}{\mu} \quad (5)$$

where:

S sample standard deviation

μ target composition of salt

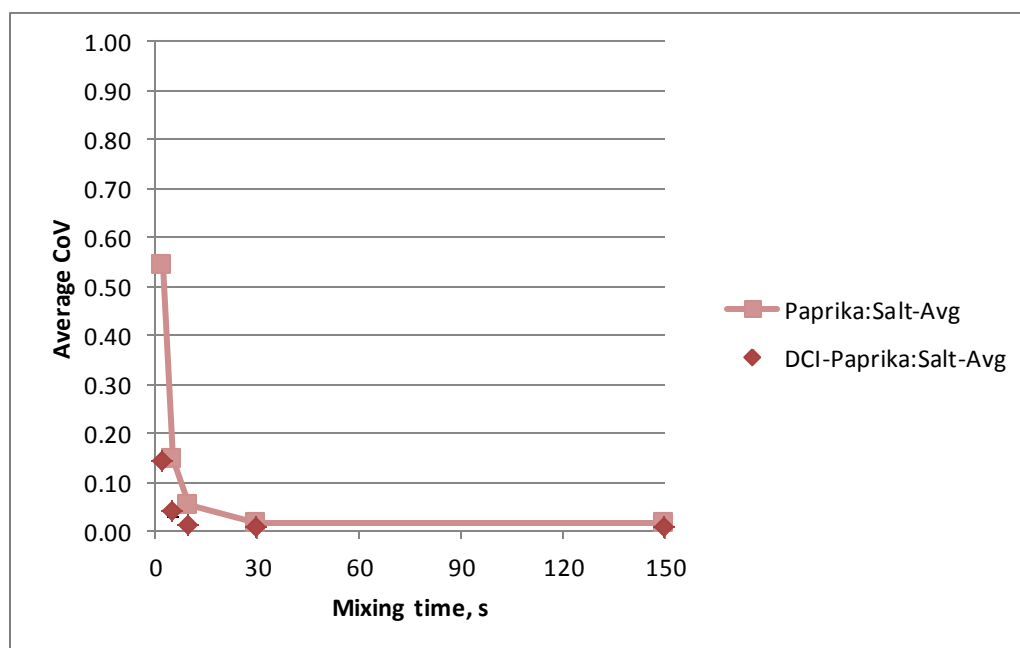
7.3 Results and Discussion

7.3.1 Well Mixing Powder Mixtures

Conductivity analysis

The powder mixes that mixed well were the Paprika-Salt (P/S) and the quaternary mix referred to as the “good mix” (GM). The mixing curves based on the conductivity data are presented in Figure 7.1 and it shows that these two mixtures mix very well. The CoV is less than 0.06 as desired, since according to company standards a CoV less than 0.06 is desired to ensure that the mixture uniformity is good (Berthiaux et al., 2008; Marikh et al., 2008). The CoV for P/S is 0.01 and for GM is 0.02 (Figure 7.1a and 7.1b). In both these mixtures very good mixture quality was observed from the 10th second onwards and the CoV decreased as the mixing time increased.

(a)



(b)

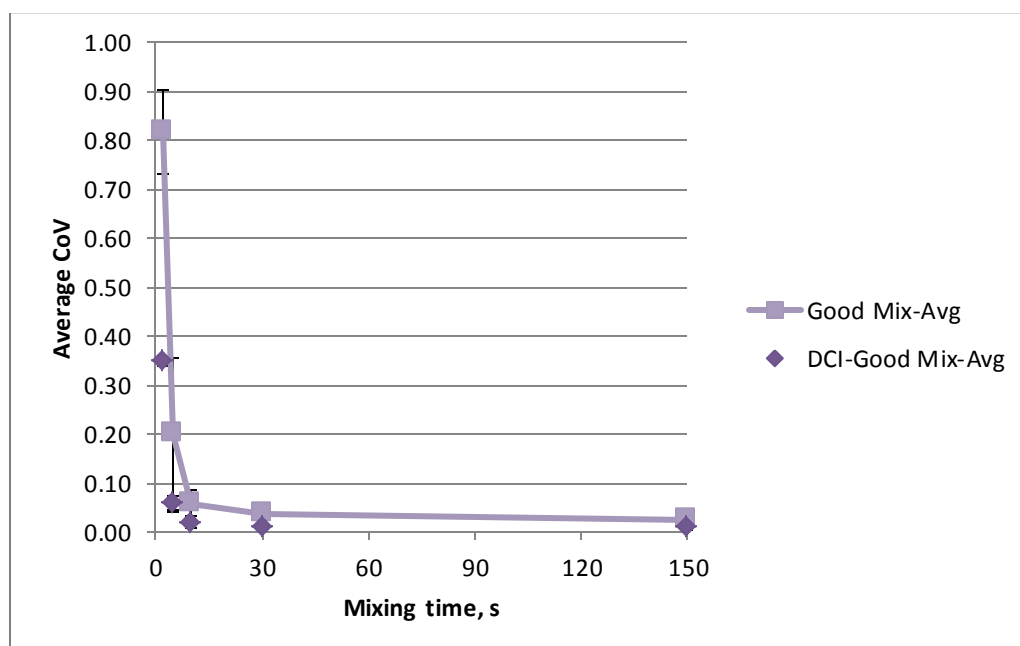


Figure 7.1- CoV plots for salt concentration and ΔE (a) Paprika-Salt mixture (b) Good Mix

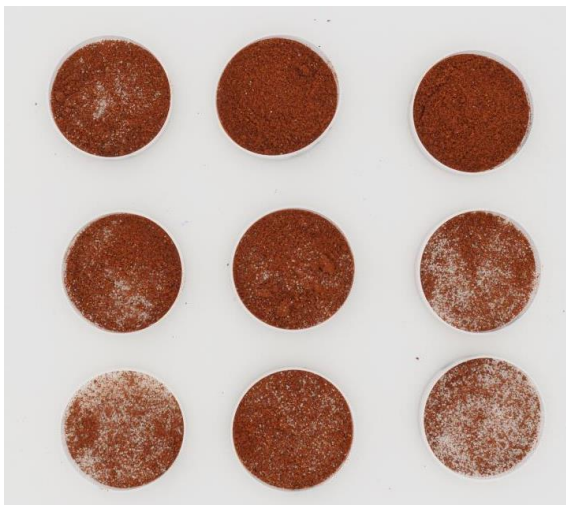
Colour analysis and comparison with conductivity

The $CoV_{\Delta E}$ obtained from the colour analysis is also presented in Figure 7.1 for both the P/S and GM mixes, which shows a strong relationship between $CoV_{\Delta E}$ and CoV. The $CoV_{\Delta E}$ values at different time points of mixing are very similar to the CoV of the salt in

the samples. Thus, there appears to be potential for applying the DCI method to assess the mixture quality of these mixes. Figure 7.2 shows the colour of P/S and GM samples taken after 2, 10, 30 and 150 seconds of mixing and it is clear from the visual observation that the powders are not well mixed after 2 seconds and appear well mixed at 30 and 150 seconds.

(a) Paprika / Salt

2 seconds



10 seconds



30 seconds



150 seconds



(b) Good Mix

2 seconds



10 seconds



30 seconds



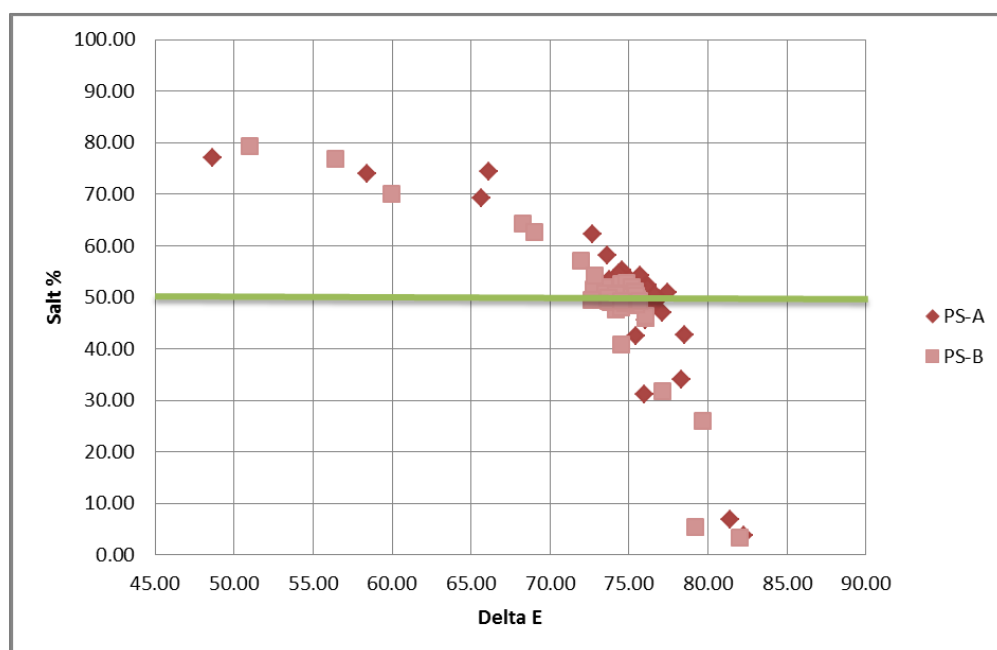
150 seconds



Figure 7.2- Progression of mixing for the 9 samples at 2, 10, 30 and 150 seconds for (a) for paprika-salt and (b) good mix

For both P/S and GM, 9 samples were taken at 5 different mixing times and each sample was measured for both colour (ΔE) and salt concentration. Consequently, for each mixing trial, there is colour and corresponding salt concentration data for 45 samples. Each mixing trial was performed in duplicate, thus there are 90 data points. A scatter plot was produced for the duplicate mixing trials for both P/S and GM and this is presented in Figure 7.3. For P/S Figure 7.3a there is a strong non-linear trend or relationship between colour and salt concentration. This demonstrates that there is good potential for the DCI method for assessing the mixture quality of P/S. Figure 7.3b shows the scatter plot for GM. There is a definite trend between colour and salt conductivity but it is not as strong as for P/S, as there is much more scatter and the presence of some obvious outliers. The reason for the greater scatter is possibly due to the fact that 2 of the components (salt and onion) have very similar colours (Table 7.3), thus it may not be possible for the DCI method to distinguish between them. Overall, the data suggests the the DCI method has potential. Even if some component powders have very similar colours, the presence of other component powders with different colours may enable the DCI method to be sufficiently effective in assessing mixture quality.

(a)



(b)

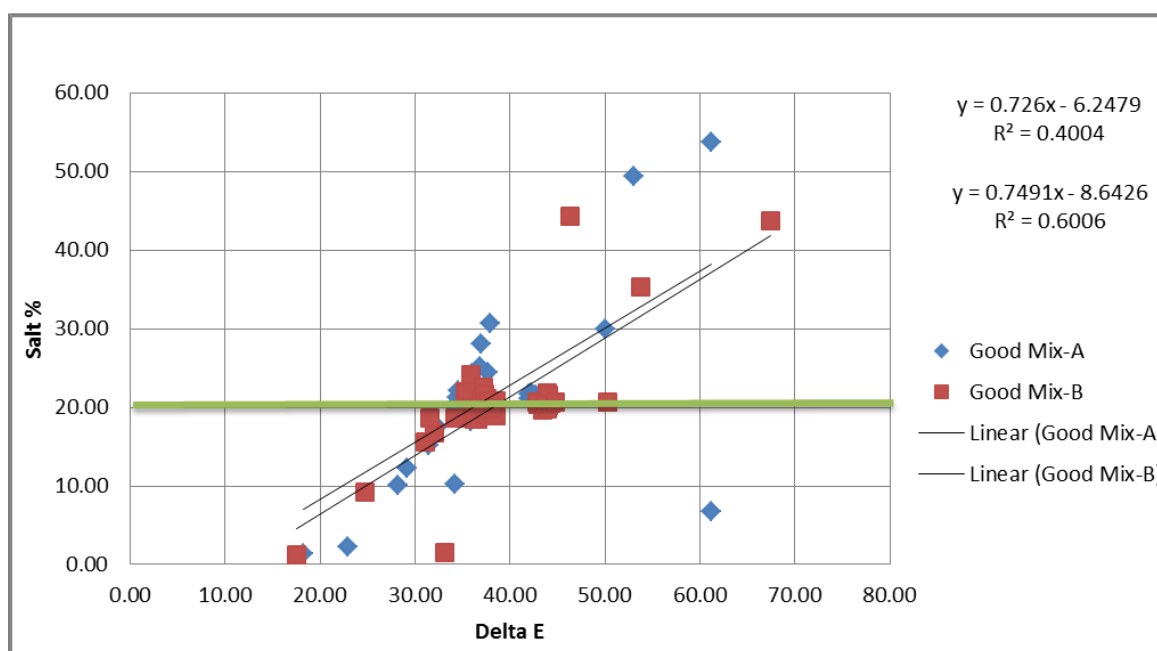


Figure 7.3- Scatter Plot for Delta E vs Salt concentration for a) Paprika-Salt mixture and b) Good Mix (*green line shows the target salt concentration in each mix)

Table 7.3- Delta E for the individual powders

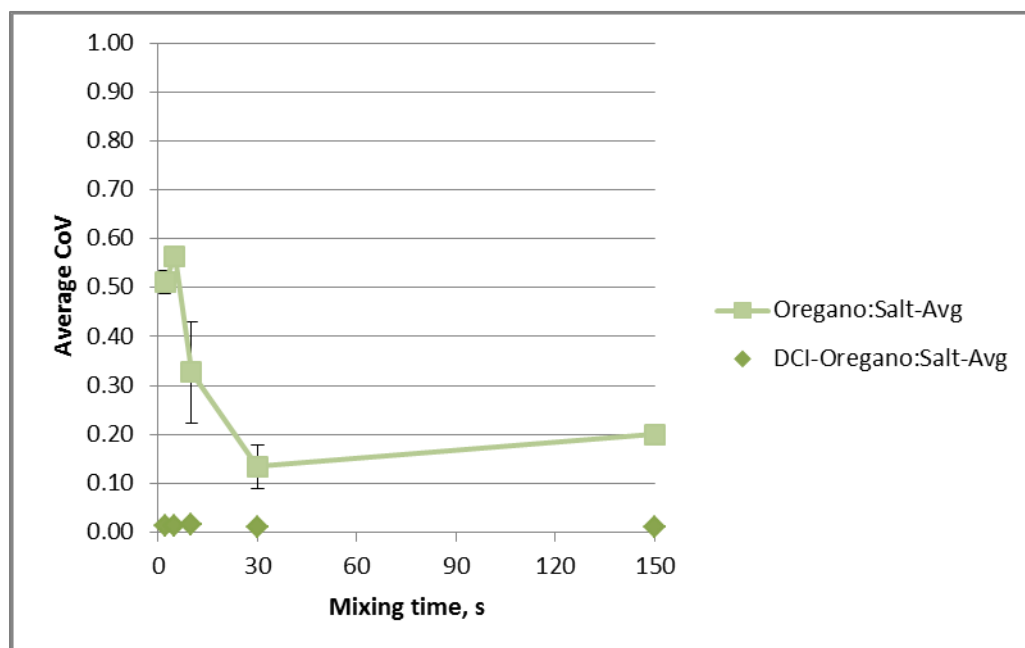
Name of Powder	Delta E (ΔE)
Paprika	78.7
Oregano	50.2
Black Pepper	50.5
Onion powder	6.7
Salt	3.8

7.3.2 Segregating Powder Mixtures

Conductivity analysis

The powder mixes that mixed poorly were the Oregano-Salt (O/S) and the quaternary mix referred to as the “poor mix (PM)”. The mixing curves based on the conductivity data are presented in Figure 7.4. For O/S mixture, the conductivity method clearly indicates that oregano and salt are segregating and do not mix well with each other, as the CoV is 0.2 even after 150s of mixing. At no time point between 0 and 150s does the mixture have a CoV less than 0.06. In the case of the PM, the CoV is also higher than 0.06 at all the mixing times and it also shows that oregano, paprika, black pepper and salt do not mix well together. This is probably due to the presence of oregano having a much lower bulk density compared to the other powders which causes the segregation tendency among the powders.

(a)



(b)

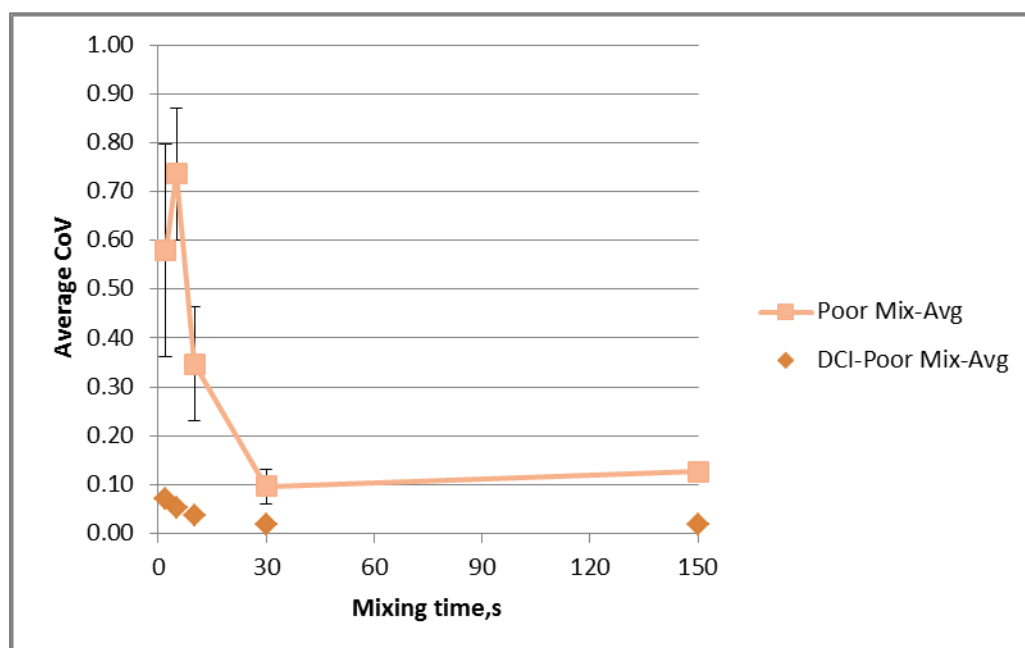


Figure 7.4- CoV plots for salt concentration and ΔE a) Oregano-Salt mixture b) Poor Mix

Colour analysis and comparison with conductivity

The $CoV_{\Delta E}$ obtained from the colour analysis is also presented in Figure 7.4 for both the O/S and PM mixes. For O/S, $CoV_{\Delta E}$ does not change over the mixing time and there is no

relationship between $CoV_{\Delta E}$ and CoV from the salt conductivity method. Visual images of the 9 samples at 2, 10, 30 and 150 seconds of mixing are presented in Figure 7.5a. There is no obvious colour difference between the images at 2 and 150 seconds. In fact, there is no obvious colour difference between the samples. They all appear to consist of oregano on the surface. Due to the leafy and bulky nature of oregano, the salt particles sieve downwards through the large void spaces between the oregano particles, thus there is little or no salt present at the surface. Consequently, the DCI only detects the green oregano particles on the surface and the small $CoV_{\Delta E}$ values represent the differences between the different shades of green of the oregano particles. Figure 7.6a shows a scatter diagram of corresponding colour and salt concentration values for samples obtained from duplicate mixing trials. It shows no relationship, thus the DCI method is not suitable for assessing the mixture quality of O/S. The major problem is not due to colour similarity between salt and oregano as there is a major difference (Table 7.3). The problem is due to segregation within the samples, that is, any salt present is sieving downwards and away from the surface. Additional trials were conducted with smaller sample thicknesses but this was not successful. At very small sample thicknesses, the bottom of the sample holder became exposed and this complicated the colour measurement. Overall, the DCI method may not be suitable for highly segregating powders, such as O/S.

For PM, there is a trend or relationship between $CoV_{\Delta E}$ and CoV , as illustrated in Figure 7.4b. Both show a reduction over the first 30 seconds. Figure 7.5b shows the colour of PM samples taken after 2, 10, 30 and 150 seconds of mixing. It is clear from the visual observation that the powders are not well mixed after 2 seconds as there is variation in the visually observed colour of the samples. At 30 and 150 seconds, the samples look more alike and the red paprika is clearly visible on the surface. Even though PM is a segregating mix, it is not as strongly segregating as the O/S mix, as evidenced by comparing their respective salt CoV values (e.g. CoV values for PM and O/S at 150 s is 0.12 and 0.2, respectively). Consequently, sample segregation is not as strong in PM. The salt, pepper and paprika are not sieving as easily through the void spaces between the oregano particles, thus some of these components are remaining on the surface and their colour is being detected by the DCI method. This may also be helped by the fact that the oregano content in PM is lower at 30% where it is 50% in the O/S mix. In

addition, the paprika and pepper have lower particle densities and are more cohesive than salt and this will inhibit particle mobility and segregation. Figure 7.6b shows a scatter diagram for samples obtained from duplicate mixing trials. There is a trend between colour and salt conductivity but it is a weak trend and not as strong as for P/S, as there is much more scatter. One contribution to the greater scatter is possibly similar to GM; 2 of the components (oregano and pepper) have very similar colours (Table 7.3), thus it may not be possible for the DCI method to distinguish between them. Another contributor to the scatter is segregation tendency of the mixture. However, similar to GM, even if some component powders have very similar colours, the presence of other component powders with different colours may enable the DCI method to be sufficiently effective in assessing mixture quality. Overall, Figure 7.4b and Figure 7.5b, in particular, suggest that the DCI method could still have potential for assessing mixture quality of PM.

(a) Oregano / Salt

2 seconds



10 seconds



30 seconds



150 seconds



(b) Poor Mix

2 seconds



10 seconds



30 seconds

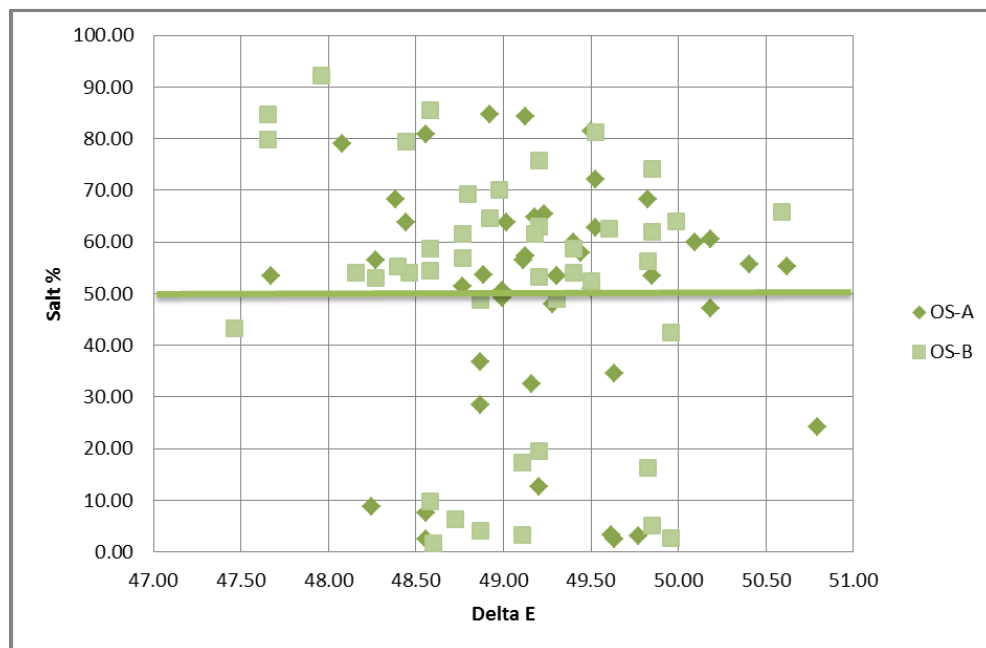


150 seconds



Figure 7.5- Progression of mixing for the 9 samples at 2 and 30 seconds for a) for oregano-salt and b) poor mix

(a)



(b)

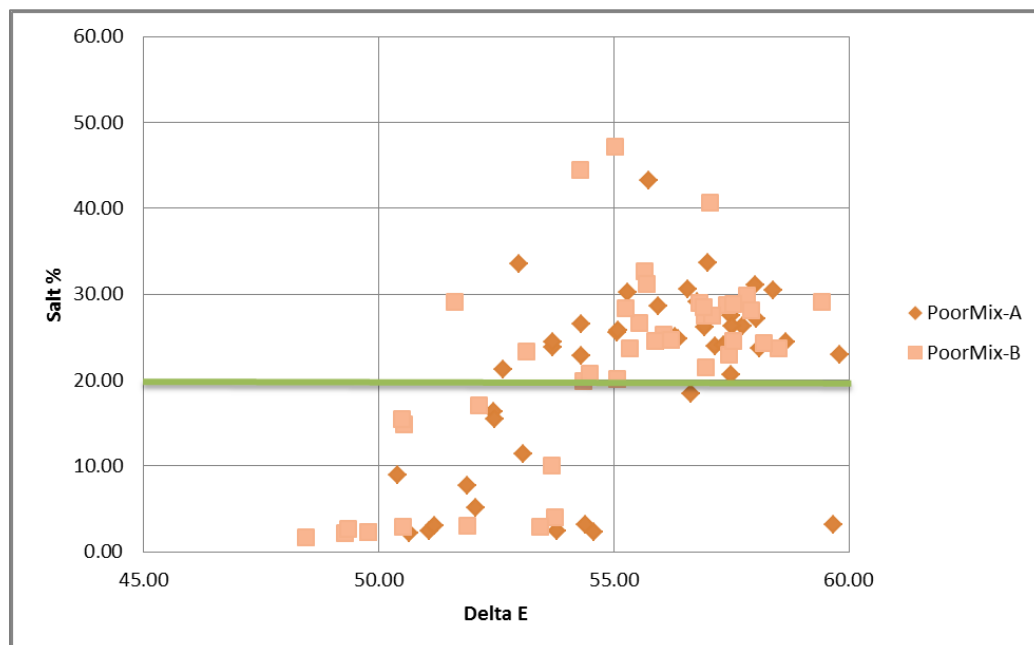


Figure 7.6- Scatter Plot for Delta E vs Salt concentration for a) Oregano-Salt mixture and b) Poor Mix (*green line shows the target salt concentration in each mix)

7.4 Conclusions

The DCI method, DigiEye, was applied in this study to investigate its potential for assessing the mixture quality of spice mixes by comparing it to a salt conductivity method. The DCI method worked very well for assessing the mixture quality of the P/S binary mix, which was a non-segregating mix and possessed large differences in colour between the red paprika and white salt. The DCI method did not work at all for the O/S binary mix, even though there was a large colour difference between the green oregano and white salt. The reason was due to the highly segregating nature of the component powders within the samples taken. The net effect was that any salt present in the samples sieved downwards from the surface and the DCI method was measuring only the colour of oregano on the surface.

For both quaternary mixes, there is potential for applying the DCI method, although the relationship between colour and salt concentration was not as strong as P/S. The reason for this is in-part due to two of the components having very similar colours, which the DCI method could potentially not distinguish. However, it could be argued that in multi-component mixes, such as quaternary mixes, the influence of two components having very similar colours could be partly overcome by the other components having different colours. Consequently, the DCI method may still be effective even if some of the components have very similar colours.

One of the quaternary mixes (PM) was a segregating mix but still had potential for using the DCI method even though there was no potential for the O/S mix which was also a segregating mix. This was most likely because PM was not as strongly segregating as O/S due to the powder properties of the non-oregano powders and also because it had a lower oregano content. The net effect was that the non-oregano powders did not totally segregate from the surface and were still visible for colour measurement by the DCI method. Overall, the DCI method shows some potential for assessing the mixture quality of powders, including spice mixes, provided there are sufficient colour differences between the components and the powders are not strongly segregating.

CHAPTER 8

GENERAL CONCLUSIONS AND RECOMMENDATION

8.1 General Conclusions

From the literature review, it is clear that mixing process is more complex than it appears to be. In order to understand mixing thoroughly it is not only enough to know the mixer properties and operating conditions but also to gain knowledge about powders and their interaction with other powders as well. As a consequence, it is also important to understand which kind of mixer is most suitable for that particular kind of powder. A very important step that follows mixing is the technique used to analyze the quality of the mixtures. This is decided carefully based on the type of product manufactured and its final application. Studies suggest use of image analysis to evaluate MQ but this often uses high level statistics which may not be easily adoptable by industries and the studies which use thief probe method for sampling and MQ analysis pose challenges to sample easily without disturbing the powder bed. Mixers such as Nauta and Paddle agitator have been largely ignored for studying dry mixing of powders. Most of the experimental and modelling work on mixing of powders has been done using the tumbler mixer. Since tumbler mixers are relatively simpler in operation and easier to sample as compared to the convective mixers most researchers focus on trying to make empirical equations for these mixers. The understanding of convective mixers is very limited even though these mixers have versatile applications in the industries (Muzzio et al., 2004). Flow patterns of powders can be complex even for simple mixing devices (Muzzio et al., 1997) this causes an additional challenge when studying mixing in the convective blenders.

Therefore, although convective mixers are one of the commonly used mixers in the industry for manufacture of powder mixtures, they have seldom been reported in the literature for studying the mixing of powders at a lab scale due to challenges posed with sampling. In this work a paddle mixer was used to study dry mixing of food powders in

which sampling and MQ analysis procedures using DCI and conductivity methods were applied.

The first part of the study aimed to use a novel technique to evaluate MQ of binary mixtures. The digital colour imaging method used in this work showed promising results for application by industries to evaluate MQ. It can evaluate the MQ of binary mixtures, which has significant differences in their colour. It is easy to use and consistent in its performance and does not require background lighting correction or treating of the image using special software. However, the components used should have a significant difference between their colours. Also depending on colour difference for each type of mixture there is a range of composition up to which the method can detect variances between the sample mixedness.

Studies done in chapter 5 showed that the proportion of powders affects the mixture quality of powders that are difficult to mix. For good mixing paprika and salt the mixture quality was not influenced by the ratio of powders used in the range of 20 to 80% salt. For the almost ideal mixing systems- sugar and salt the proportion of these powders did not have any influence on the MQ and they achieved very good mixture quality for the range studied. Oregano:salt mixtures tend to disimprove when the oregano content is increased in the mixture, this is due to the larger void spaces of the oregano leaves. Thus it is seen that ratio of powders has a profound influence on powder systems that are already difficult to mix as compared to ones that mix easily.

Both the good mixing and poor mixing systems were influenced by the water content of the powders- paprika and oregano. For oregano:salt mixture, the increase in moisture of oregano helped to bind the salt particles to its surface almost creating something similar to ordered mixtures whereas for paprika:salt mixture, the presence of around 30% of water in paprika slowed the mixing process of paprika and salt. At higher water activity paprika became cohesive in nature and the bonds between paprika particles had to be broken to enable proper mixing with salt. Thus although the final MQ of paprika:salt was still better than MQ of oregano:salt, the time required was longer compared to other mixing trials of paprika:salt. For oregano:salt the increase in moisture helped to improve the MQ of the mixture due to formation of cohesive bonds. Flowability data for both oregano and paprika shows that at higher water activities, both powders become

cohesive in nature. Paprika changes from an easy flowing to highly cohesive powder when the water activity is increased. When the water content of salt is increased, both paprika and oregano have difficulties in mixing due to the cohesive nature of the salt. In case of paprika:salt mixture, the powders could not mix after 10 s of mixing due to the extremely cohesive nature of salt that resulted in caking of the paprika:salt mixture. For oregano:salt mixture the MQ was as bad as the MQ for oregano:salt trials conducted at lower water activities (30% RH). However, in this case the poor MQ was a consequence of the difficulty to mix cohesive powders as compared to the poor MQ caused due to segregation of powders for trials conducted at 30% RH.

In chapter 6, it is seen that both particle size and bulk density affect the MQ of the powder mixtures. In literature, usually particle size has been considered as the primary factor that determines MQ for powders. Trials performed using paprika:salt and potatostarch:salt powders showed that although size has an effect on the MQ of powder mixtures, it did not worsen the MQ to a large extent. The MQ at the end of mixing for size ratios as large as 16 was still at a satisfactory level and had a CoV equal to 0.06. This was due to the coating effect of particles for the large size ratios. The larger size powder particles were coated by smaller sized particles which helped to provide sufficient MQ and reduced the segregation tendencies in these mixtures. On the contrary, when powders with similar particle size and differences in bulk density were mixed, the bulk density had a major influence on the MQ. When bulk density ratios more than 6 were used, the MQ worsened leading to segregation of powders. For bulk density ratios within 3.5, very good mixing was observed. For higher bulk density ratios increased voidage between the particles led to the falling down of regularly shaped smaller dense particles through the void spaces of the larger particles causing segregation. A good balance of particle size and bulk density must be considered when choosing powders to avoid segregation tendencies. Differences in shape should also be minimized since shape also has an impact on the ability to create voidage between particles.

Finally from results in chapter 7 it is seen that both the methods used to evaluate MQ discussed in previous chapters; the DCI as well as conductivity analysis works for powders that mix well. However, for powders such as oregano and salt which have a tendency to segregate it is not possible to use the DCI technique since it only does a surface level analysis of MQ. Oregano:salt mixtures undergo vertical segregation in the

sample holder and therefore only oregano leaves are analyzed for MQ by colour analysis method which results in a low CoV. Similarly for poor mixing quaternary mixtures, when the digital colour imaging method is used for MQ analysis it gives very low CoV because of the presence of similar coloured powders as well as the segregation tendencies of the powders used. In such cases it is not advisable to use the DCI technique as it gives incorrect information about the ability of powders to mix. In case of the good mixing powders both conductivity as well as DCI methods gives similar results that suggest that the MQ is good and either of the techniques can be used. Here it may be good to use the colour-based method not only to measure the MQ of the mix but also to decide a time when the desired colour for a certain product can be achieved.

In this study, it was observed how two different techniques could be applied to measure the mixture quality of powder mixtures based on the type of powders used. The effect of different properties of powder such as composition, water content, particle size and bulk density was investigated and the findings clearly indicate that the final MQ is determined by a combination of different properties of the powder which contribute towards a certain mixed state of the powder mixture. Of course, there are several other factors which determine the final MQ such as the type of mixer used, operating conditions and the surrounding conditions during the mixing process. More experimental studies are required that compare different operating conditions on different types of mixers and different types of powders to form a mapping of the powder properties to the mixing conditions as well as predict the MQ for development of new mixtures.

8.2 Recommendations

In this work two methods to evaluate MQ were presented and their limitations and advantages were discussed. Also, the effect of powder properties on MQ was studied and the results presented can be applied to other powder systems similar to the ones studied in this work. However there is still scope for improvement in future and more trials in a similar direction can help extract more information to understand the mixing mechanisms better. Some suggestions for the future work have been discussed below:

a) Type of powders

Only two types of powder systems – good mixing and poor mixing i.e. paprika:salt and oregano:salt have been primarily studied in this work. Although studies have been done using other binary powders in one part of the study, main focus has been on paprika:salt and oregano:salt mixtures. Therefore, results from this study can be applied for powders that have similar characteristics such as oregano and paprika only. Since powders have different shapes, surface characteristics and other properties such as particle sizes, density, cohesivity, structure etc., to get a better understanding and validate results from this study it is important to use other different types of powder systems and combinations for experimental trials.

b) Method for analyzing MQ

The methods used to analyze MQ have its own limitations, one of the biggest limitation being that salt is a mandatory component for all the mixes so that conductivity method can be used. New methods which are non-destructive such as NIR should be applied for evaluating MQ so that any kind of powder can be used.

c) Multi-component mixing trials

Since spice mixtures typically consist of 10-14 ingredients, lab scale studies need to use similar conditions as that of industrial level of mixing. The lab-scale trials should also consist of similar number of powders as used in the original mixture, and should be operated under the same conditions as that of the factory mixer. Some studies suggest that when more powders that have a larger particle size distribution are used the tendency to segregate is reduced. This suggests that binary mixing trials are insufficient to correctly predict the behavior of certain types of powders in larger systems.

d) Particle size

We observed that oregano:salt was a highly segregating mixture under normal room conditions. It is known that particle size differences are the primary cause for segregation. The size difference between oregano and salt used in this study was high, therefore it would be interesting to grind oregano into smaller particle sizes and mix it with salt to check if this improves MQ.

e) Characterization of powders

The basic property data of many food powders is missing. A detailed classification of powder property data based on size, colour, particle, bulk and tapped density, shape, cohesiveness, moisture content and moisture adsorption characteristics can be useful to design powder mixtures in a better way.

f) Pilot scale studies

In this work, a Froude number 0.65 was used for all the trials. In industries a Froude number closer to 1 is preferred but since 0.65 was already very quick to provide good MQ only this condition was used in this study. It would be interesting to conduct the same trials in a pilot scale mixer with same operating conditions and check what deviations occur. Also it would be interesting to repeat the study for Froude number 1 at lab scale as well as pilot scale. This can help in forming a relation between the lab scale and pilot scale trials for paddle mixer and may provide valuable input for creating models.

g) Sampling after mixing

A common problem faced by industries is demixing of powder mixture during packaging although the powder mixture quality inside the mixer is good. This segregation may be caused due to vibration or external forces. Experiments should be conducted to investigate how the MQ of powder mixture is affected during the batch emptying of the mixer.

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