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## An Investigation of Spray-Freezing and Spray-Freeze-Dryings

By

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Department of Chemical Engineering

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy

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### Abstract

Drying is an important process for a variety of industries such as pharmaceuticals, food, and chemicals, and produce products with low bulk density, good shelf stability, economical storage and transport, and in some cases unique structural qualities. Of the various drying methods available, freeze-drying is the most beneficial for heat sensitive products that susceptible to thermal degradation. Freeze-drying also confers a porous structure on the material result from the voids left after subliming the ice crystals. Freeze-drying however is used mainly for high value products due to the high capital and operational costs. The cycle time of such a drier may take several hours.

The spray-freeze-drying process has evolved in an attempt to shorten the freezedrying process time. The process atomises a liquid feed to increase the heat and mass transfer surface area. The spray is then frozen in a very cold gas or a cryogenic liquid to form solid particles, which are then freeze-dried. Some processes incorporate a fluidised bed freeze-drier to reduce the drying time by forced convection heat and mass transfer.

This project aim to develop the Spray Freeze- Drying process and examine the effect of the process on the drying entities and resulting product quality, followed by modelling of the spray freezing operation in an attempt to optimise the operation. This thesis is divided into two main areas of investigations;

Spray freezing investigation as an influential on the resulting product size and structure. The experiments performed using Phase Doppler Anemometry technique to measure the particle size distributions and velocities in a specially constructed spray freezing chamber with incorporated windows. A spray freeze-drying chamber was constructed composed of three parts co-current spray freezing, gas - particle separation, and fluidisation freeze-drying unites. Successfully spray characterisation measurement was carried in both ambient and sub-ambient temperatures, producing data of the drop size distribution and velocities from refractive scattered laser PDA measurement. The technique produced valuable information about the spray size distribution and velocity, the application of this technique appear was a novel approach in the spray freezing process measurement. The result were used in the established spray freezing model derived from Pham (1984) freezing model incorporating with a recalescence stage from the Hindmarsh (2003) spray freezing model. The current model predicted the droplet freezing time, which is influenced by the droplet diameter, velocity and freezing gas temperature. The results also shows an agreement between the freezing time predicted and the PDA recognition of bursts rejected due to their possible phase change.

The spray-freezing-drying chamber was operated in vacuum conditions to produce freeze-dried whey protein powder. The powder characteristic results shows an physical properties such as density, solubility and particle sizes in comparison to spray drying and cryo-spray freeze-drying. The morphology of the spray freeze-dried whey powder is substantially different to that produced by spray drying and displays a porous microstructure. The operation of the freeze-drying unites requires an further investigation for temperature, pressure, and flow control to maintain the freezedrying.

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# Chapter 1

Introduction

### 1.1 Spray freeze-drying introduction

Freeze-drying is a dehydration process which involves sublimation of ice from frozen material and requires water to be at a temperature and pressure below the water triple point (0.01°C and 4.6 torr) (Goldblith *et al.* 1975; Mellor 1978; Jennings 1999). Freeze-drying has the advantages of handling thermo-labile materials, those are susceptible to thermal degradation and quality loses such as certain pharmaceuticals, foods, and biological aqueous fluids (Deluca 1977; Mellor 1978; Desrosier *et al.* 1979; Jennings 1999). It can also produce unique product morphology, for example the production of multi-component ceramic super conductor powder (Roehrig *et al.* 1972; McGrath *et al.* 1992).

The earliest mention of freeze-drying in history is the Peruvian Incas of the Andes who practiced the basic process of freeze-drying foods. The Incas stored their potatoes and other food crops on the mountain heights above Machu Picchu, where the cold mountain temperatures not only preserved the food by freezing, but also sublimed to dry the food. At those altitudes the low pressure and temperature the two basic requirements for sublimation - naturally existed. Some recent discoveries also found number of well-preserved mummies, which have survived for many centuries.

The scientific study of this drying method dates back to 1813 by a paper presented to the Royal Society of London by William Hyde Wollaston who pointed out the possibility of ice sublimation. Shackell performed the first clearly recorded case of preservation of a biological substance by sublimation in 1909 (Flosdorf Earl 1949; Goldblith *et al.* 1975; Mellor 1978; Jennings 1999).

The benefits of this drying method had drawn the attention of many disciplines from biological, chemical, material, to space science. During World War II, the freeze-drying process was developed commercially when it was used to preserve blood plasma and penicillin. Over 400 different types of freeze-dried foods have been commercially produced since the 1960s. The best known product is the freeze-dried coffee, which first produced in 1938, and has been commercially successful since 1954, and has been progressively

developed since then. There is now large variety of processing equipment and plants used worldwide to dry different types of material (Jennings 1999).

There are two main forms of freeze-drying found in practice:

- Ice sublimation at atmospheric pressure and low temperature. This process relies on mass transfer from the drying material surface to a very dry gas. It is a lengthy process and requires a large volume of the carrier medium in the case of gas.
- II. Ice sublimation under low pressure and temperature, below water triple point, see figure (1-1). This process, though it is a faster than the first one, case but it takes hours (even days in some cases), and it requires a detailed process control procedure to complete the operation successfully (discussed later).



Figure 1-1: Phase diagram Ice-Water-Steam. (www.chemicalogic.com).

A frequent misunderstanding of the freeze-drying process is that ice sublimation does not take place unless the total system pressure is below the triple point pressure. However it is known that ice sublimation occurs on a very large scale in Antarctica at atmospheric pressure. During strong winds, surface ice is blown loose, becomes airborne and sublimes (Mann 1998). Dehydration of unwrapped food stored in domestic freezers is another common example of atmospheric freeze-drying. In 1959, Meryman investigated the possibility of freeze drying without a vacuum and he confirmed that ice sublimation in freeze-drying is dependent on partial pressure of vapour gradient of the dried material and the surround rather than the system's overall pressure (Meryman 1959). Since then, atmospheric freeze-drying, had been investigated over the last 40 years by different researchers, most of them focusing their investigation on one or few aspects of this drying technique. Interest extended to other aspects of this new drying method, when Woodward in (1963) investigated the economics of this drying technique using meat samples in an atmospheric freeze drier, and compared their production cost with the conventional freeze drier. His conclusion was, that freeze drying without a vacuum is cheaper than conventional freeze drying in term of capital cost, while the operational cost is almost equal for both processes (Woodward 1963; Noyes 1968; Goldblith et al. 1975; Mellor 1978). Malecki, et al. (1970) reported that the rate-controlling step for water vapour removal in freeze-drying is diffusion through the solid specimen (Malecki et al. 1970). In the frozen matrix the vapour pressure is higher in the small ice crystals, tend to migrate to the lower vapour pressure surrounds (Strumillo et al. 1998). Therefore, reducing the frozen matrix size by forming small particles would increase the mass transfer rate of the drying process (Heldman 1974). Mumenthaler and Leuenberger (1991) used on some of these findings to develop an Atmospheric Freeze-Spray Drying System with integrated fluidised bed, see figure (1-1). They managed to achieve successful drying results with short drying time, less than two hours, as well as a good product quality (Mumenthaler et al. 1991 2000).

This atmospheric spray freeze-drying process was described as a controlled operation of rapid spray freezing, achieving porous structured particulates from convectively accelerated atmospheric sublimation. However there is a novel opportunity of further improvement in the spray freeze-drying process by applying the partial vacuum to further accelerate the process, using the spray freezing and low pressure fluidisation in an integrated process.



Figure 1-2: Schematic diagram of the atmospheric spray-freeze-drying apparatus (Leuenberger 2002): 1. Spray tower, 2. Spray nozzle, 3. Heating device, 4. Spray solution, 5. Filter system, 6. Flap, 7. Air-filter, 8. Fan, 9. Refrigerator and condensers,10. Heating system, 11. Bypass pipe and 12. Spray air for spray nozzle.

The research has the following aims:

- To design and construct a spray freeze-drying experimental rig, which can be used as a basis for further process development, and as a mean of producing spray freeze dried sample.
- 2) To examine the physical, functional, and morphological properties of particulate materials which have been spray freeze-dried, and compare to those obtained from spray drying. The effect of spray freezing in gas and in liquid nitrogen is also investigated.
- To investigate the spray freezing process. Spray freezing is a critical to the structure of the resulting particles as the distribution of the ice crystals directly corresponds to

porous region in the dried product. The connectivity of the ice crystals pores also important on the kinetics of the sublimation process. This has therefore been studied in some depth using Phase Doppler Anemometry (PDA) to characterise the spray, by obtaining insitu drop sizes and velocities of the spray bulk. This is used to provide data for a simple model of spray freezing.

Brief summaries of the topics of the remaining chapters of this thesis are as follows:

- Chapter 2: This is the literature review of processes which have features in common with SFD process, namely spray drying, fluidisation and fluidised bed drying, conventional freeze-drying and atmospheric freeze-drying, as well as spray freeze-drying itself. The process operations and related mathematical models are described.
- Chapter 3: This is a descriptive report on the design and construction of the experimental rigs used in this research. The material included introduces the conceptual design of the spray freeze-drying apparatus and further information on individual unit operations, describing the justification of the choices made. The chapter is sub divided into three experimental rig design sections; (i) the spray freezing characterisation rig, (ii) the spray freeze-drying rig, and (iii) the cryo-sprayfreeze-drying rig. The operational procedures and problems encountered with building and commissioning were also highlighted.
- Chapter 4: Here the various experimental methods to characterise both the liquid feed and resulting particulate products are described. Liquid feed tests include measurements of density, viscosity, surface tension and temperatures of phase transitions by Differential scanning calorimetry DSC. Particulate characterisation tests including moisture content measurement, density, porosity, particle sizing and morphology (SEM).
- Chapter 5: This chapter reports experiments preformed using the established technique of Phase Doppler Anemometry (PDA) to analyse the spray freezing process by measuring particle size and velocity at various distances from the spray nozzle. The possible use of the technique as a probe for detecting phase change in droplets is also investigated. The chapter conclude with results from a simple

spray-freezing model to predict freezing time using velocity data from the PDA experiments.

Chapter 6: This chapter describes the results of experiments to produce and compare dried particle products (sucrose, whey and coffee) from three drying processes:

- (i) Spray drying,
- (ii) Cryo-spray freeze-drying (freezing in liquid nitrogen), and
- (iii) Spray-freeze-drying (freezing in gas).

Chapter 7: Conclusion and recommendation for future work.

# Chapter 2

Literature Survey

An Investigation of Spray-Freezing & Spray-Freeze-Drying

#### 2.1 Introduction

Drying is the removal of moisture by either evaporation of a liquid or sublimation of solid to the vapour phase due to the combined action of heat and mass transfer. Firstly it is worthwhile to consider the reason why products are dried. The purpose in drying comes mainly from its benefits in economical, quality and functional improvement of substances, and for extending some products availability, in the following ways:

- Preservation of crops (e.g. wheat, rice) so they can be used throughout the year to ensure an even supply of food away from the harvest season. In the case of fruit and vegetables these confers a quality change (e.g. raisin prunes, strawberry and others) which results in entirely different products to the fresh. Drying of fruits and vegetables has been traditionally carried out to preserve the produce throughout the year and not limited to their seasonal and/or geographical availability (MacCarthy *et al.* 1986), for example figs, raisin, strawberry, and others.
- Reduction of the storage space and transport costs due to the removal of water, as in drying of liquid material such as milk and coffee (Masters 1991).
- Not least important is the functional and quality improvement of substances by drying, like the freeze-drying of multi-component pre-ceramic ultra fine porous powder (Roehrig *et al.* 1972; Hampden-Smith *et al.* 1999), and freeze drying of coffee for easy re-hydration and volatile retention (Desrosier *et al.* 1979).
- Preservation of bio-materials which degrade over time due to the action of microorganisms and enzymes which require moisture to function. In addition there is the production of high quality thermo-labile material, such freeze-drying of vaccines and drugs (Deluca 1977; Jennings 1999).

Drying process, however are often poorly understood and their operation can some times resembles an art rather more than a science (MacCarthy *et al.* 1986; Jennings 1999). Although drying methods have been extensively researched, almost all practical design work uses empirically based methods to predict drying rate. Theoretical models are generously unreliable due to the complexities of moisture transport within solids (Chune Yao *et al.* 1976; Boeh-Ocansey 1983; Liao *et al.* 1990; Strumillo *et al.* 1998). There are large number of drying methods used either in batch or continuous mode setup on both industrial or small An Investigation of Spray-freezing & Spray-Freeze-Drying

scales operation. The drying methods are been continuously upgraded and modified to suit new applications (Strumillo *et al.* 1986). These include electric dehydrator, microwave ovens, tunnel dryers, conveyer band dryers, rotary drum drier, vacuum evaporators, spray drier, and freeze-drier. The selection of drying method is very much dependent on the on the dried material and the product in question. (Brennan 1990). As relatively a little work has been preformed on spray freeze-drying. This literature survey will also consider other processes that have a features that are relevant to this study, the technique involved and aspects found in other drying operations namely spray drying, fluidised bed drying, freeze drying and gas dehumidification to be combined in one system.

#### 2.2 Spray Drying

Spray drying involves the atomisation of a liquid feedstock containing a dissolved solid into a spray of droplets and contacting these droplets with hot air in a drying chamber. Evaporation of moisture from the droplets leads to the formation of dry particles. The resulting powder is then discharged continuously from the drying chamber, where it may be further treated e.g. agglomerated. The operating conditions and dryer design are selected according to the drying characteristics of the product material (Marshall 1954; Masters 1991), and require careful control of temperature and airflow.

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Spray drying has been implemented since the early quarter of the 19<sup>th</sup> century; however, it did not achieve extensive industrial use until the 1950's. It has been used in variety of industries, mainly chemical, pharmaceutical, and food. The success of this process derives from the ability to rapidly dehydrate liquid feeds of an aqueous, solution, and slurry nature, involving good size, dehydration, and product quality control. The ability to operate in continuous production allows high production rates (Marshall 1954; Strumillo *et al.* 1986; Masters 1991).

The shape of most spray-dried particles is spheroid, which gives the end product fluid-like flow properties that makes many downstream operations (e.g. packaging, filtering, and handling) easier and less costly. Spray drying produces the most homogeneous product for multi-component solution/slurries; each particle will have the same (dry basis) chemical composition as the mixed feed. The surface area produced by atomisation of the liquid feed enables a short gas residence time, ranging from 3-40 seconds depending upon the application, which minimises thermal degradation. The positioning or the mounting of the atomiser is crucial in the design of the spray drying rig, as it must allow sufficient spray air contact without contacting the spray with the chamber wall. In an efficient design the spray will not contact the chamber wall and hence the dryer chamber remains dry.

### 2.2.1 Process Principles

The main advantage of dehydration by spraying is that spraying operation creates a very large surface area to volume ratio by atomising the liquid feed into a hot or/warm environment where evaporation of the solvent (water) takes place. The atomisation increases the heat and mass transfer surface area, which rapidly reduces the drying time. Spray drying process involves four operational stages (Marshall 1954; Brennan 1990; Masters 1991).

- 1. Atomisation of the liquid to form droplets.
- 2. Contacting the droplets with the drying gas.
- 3. Evaporation of moisture from the droplets.
- 4. End product collection and recovery.

These operations described briefly viewing the interests of the design and operation relative to the current research.

### 2.2.2 Atomisation

The atomiser is the heart of the spray drying process, consequently determines the droplet size distribution that influences the drying rate as well as the product motion and the product size distribution (Marshall 1954). Atomisers are of various types and characteristics such as rotary atomiser, pressure nozzle, air-assisted nozzles, sonic, rotary cup, and electrostatic atomisers. Their choice and design varies according to the specific purpose of the drying or operation process built for. The selection of a specific atomiser for an operation is generally based criteria set to accommodate the needs of the production, the key features considered in when selecting the atomiser are

• It should be cheap and low maintenance, with simple settings and easily operated finally flexibly mobile.

- Have the ability to handle a variety of feed types (aqueous solutions suspensions), provides close performance over their range of physical properties and concentration.
- Provides a uniform particle sizing and small size distribution.
- Be capable of instant atomisation or droplet disintegration on the tip of the atomiser.

The mechanism of the spray formation in this process is based on the stability and collapse of liquid-jet systems (Marshall 1954; Masters 1991). The break up of the liquid feed results inertia forces created by imposed high velocity that overcome the surface tension and viscosity resistance of the liquid feed. This instability is imposed on the liquid feed through the atomiser, which leads to the liquid disintegration when crossing the atomiser outlet orifice into ligaments (tearing). These segments further disintegrate into droplets upon the force of contacts exerted from the surrounding gas on these ligaments (Marshall 1954; Masters 1991; Perry *et al.* 1997). In general, the disintegration of ligaments and the spray formation is not uniformly co-ordinated which results in range of droplet sizes in the spray. Producing droplets of specific size and surface area by atomisation is a critical step in the spray drying process. Most atomising techniques produce a wide spread of particle sizes.

The degree of atomisation, spray uniformity and droplet sizing depends on the type of atomiser and feed applied in the process. The most commonly employed atomisation techniques are; pressure nozzle, pneumatic twin fluid atomisers and rotary atomisers. In this research only the pressure and twin fluid spray nozzles are of interest.



Figure 2-1: Fluid disintegration by atomisation as been seen by Dombrowski & Johns. (Perry et al. 1997).
The simple description of the atomisation mechanism in these nozzles is theorised by the formation of drops upon the breaking of jet due to forces acting on and within it. Castleman suggested that the degree of atomisation is controllable by the relative velocity of the atomised feeds jets and its stability, which is function of Reynolds number. The jet tendency for disintegration is dependent on the liquid viscosity, density, surface tension and jet size (Marshall 1954).

In pneumatic atomisation the drops are formed from collapsed ligaments and thin films of liquid resulted from a mixed jet of a liquid and compressible gas. Castleman utilised pneumatic atomisation to Rayleigh's theory of jet breaking up, and it is entirely influenced by the liquid physical properties on the drop disintegration. For a hydraulic nozzle atomisation is a result of pressure energy conversion within liquid bulk to a kinetic energy of a moving thin sheet of liquid. The physical properties of the liquid and the frictional effect of the medium into which the sheet is discharged affect the break up of the thin sheet (Marshall 1954; Masters 1991).

#### 2.2.2.1 Pressure nozzle atomisation

In this nozzle the fluid is forced through an orifice under pressure to create a spray. The pressure energy within the feed converted into a kinetic energy of moving sheets of liquids. These sheets disintegrate into droplets under the influence of the medium, which it is discharged into (Masters 1991). A feed pump supplies the pressure energy required for atomisation. Typically piston-type positive displacement or diaphragm pumps are used, and depending on the liquid viscosity the operating pressure of these pumps ranges from 0.3 to 6.9 MPa (Perry *et al.* 1997). Pressure nozzles differ from each other by the type of feed input and the shape of the orifice, see figure (2-2). The most commonly used type is the swirl type atomiser.

The main characteristic advantage of this nozzle is the capability of atomising viscous liquids. This nozzle produces a reasonably narrow spray angle, which is should controlled to minimise build up of the product on the wall of the chamber. This narrow spraying angle also helps reducing the spray chamber capital cost. The average particle size produced for a given feed is primarily a function of the flow through the nozzle, which is linked to the nozzle orifice pressure drop. The disadvantages on the other hand are the production of spray with a wide droplet size distribution. It also requires routine changing of the internal pieces, usually made of tungsten carbide, as the feed pressurisation through the orifice causes abrasion on the nozzle design. The other disadvantage is risk of blockage at low feeding pressures (Marshall 1954; Masters 1991).



Figure 2-2: A schematic diagram of two types the pressure nozzle (Masters 1991).

- a) Swirl Type Pressure Nozzle
- 1. Nozzle Body,
- 2. Orifice insert,
- 3. Swirl chamber,
- 4. End Plate,
- 5. Screw pin.

- b) Slotted Type Pressure Nozzle
- 1. Orifice insert
- 2. Nozzle cap,
- 3. Grooved core insert



Figure 2- 3: Pneumatic Nozzles (Masters 1991). (a) Two fluid internal mixing nozzles, (b) Two fluid external mixing nozzle, (c) Three fluids external-internal combined mixing nozzle.

### 2.2.2.2 Pneumatic two-fluid nozzle atomisation

This nozzle works by direct impingement of the liquid feed with a pressurised fluid stream that causes the formation of a spray, usually compressed air or gas. This gas provides the atomisation energy. The contact of involved fluids can take place either inside or outside the nozzle body (Marshall 1954; Masters 1991; Perry *et al.* 1997).

The two fluid nozzle, (also know as the pneumatic nozzles), is characteristically used for the production of fine droplet sizes, as low as 10-30  $\mu$ m, and generates a narrow particle size distribution. The average particle size produced for a given feed is primarily a function of the liquid flow per nozzle, and the compressed gas rate and pressure (Masters 1991). The spraying angle produced by this nozzle type is a narrow (17-22°), but the control of the spray angle is limited. The nozzle uses any type of feed pumps for inputting either feed, however it is capable of drawing the liquid feed in by the negative pressure created by the gas flow. These nozzles are used widely for a small scale production plants and operation due to their capability of atomising small amount of feeds and creation of relatively uniform droplet size distribution.

The disadvantages associated with the twin fluid nozzle are mainly the requirement of periodic changing of the air and liquid caps, and this nozzle is the least energy compared to efficient other alternative atomisers, however the capital cost can be lower. The nozzle is also introduce a second gas flow into the chamber, which can interfere with the drying capability of the hot gas.

### 2.2.2.3 Rotary atomisation

In this atomiser the spray is produced by the effect of centrifugal forces acting on a sheeted liquid fed on to a spinning disc, of different designs as illustrated in figure (2-4). The feed extend in a thin sheet to the periphery of the disc and then disintegrate some distance a way from the nozzle (Masters 1991; Coulson *et al.* 1996).



Figure 2- 4: Rotary atomiser (Coulson *et al.* 1996). (a) sharp edge -flat disc atomiser, (b) bowl atomiser, (c) vane disc atomiser, and (d) air-blast bowl atomiser.

This atomiser type is more versatile to handle different type of liquid viscosities, and producing reasonable size distribution than the pressure nozzles. Some of the disadvantages associated with this atomiser are the large spraying chamber requirement due to the spray wide coverage area of the spray, and the maintenance complexity. Also it requires a rotary driving motor that is complicate the design of the atomiser (Masters 1991).

### 2.2.3 The Drying Chamber

The most important function of the spraying chamber is providing the spray with a sufficient residence time to accomplish the drying process with no quality degradation or unwanted wall deposition. This chamber can be fabricated from a variety of materials, selected on the basis of easy cleaning, chemical and corrosive resistance, efficiency, cost, and strength (Masters 1991). The introduction of hot gas into the chamber proceeds via a dispersing unit as seen in figure (5-7). Its main task is distributing the gas flow through the chamber uniformly.

### 2.2.3.1 Gas-spray contact

The contact between the spray droplets and drying air controls evaporation rates and product temperatures in the dryer, therefore, this contact within the chamber must be chosen to suite the dried material and the atomiser used. There are three modes of contact (Marshall 1954; Masters 1991; Coulson *et al.* 1996) illustrated in figure (5-6).

- In co-current operation, the drying air and spray moves in the drying chamber in a same direction. Here it is possible for the gas flow disperser to influence the droplet size distribution from the atomiser. This mode of spray gas contact is usually preferred for heat sensitive materials as the hottest gases contacts the wettest drops which are protected by evaporative cooling.
- In counter-current operation, the drying air and spray moves in the drying chamber in opposite directions. This mode of contact is the most energy efficient setup and used for non-heat sensitive materials.
- Mixed flow, the drying air and spray movement through the drying chamber experiences a combination of both co-current and counter-current flows, the design entail a two directions airflow and the product is unidirectional. This mode of gas product contact is know to offer a high air to product ratio that is ideal to sweep the cohesive material of the walls in a cyclonic motion, but the draw back is the higher entrainment of the products to be recovered.

# 2.2.4 The Dry Product Discharge & Product Recovery

It is necessary to reclaim the fines from the gas stream for both economical and environmental reasons. There are two major fine and product recovery units in wide spread (Brennan 1990; Masters 1991; Perry *et al.* 1997).

# 2.2.4.1 Filter Bag

This unit operates by separating the particles from the airflow in the two-phase flow inlet, the separation efficiency is dependent on the filter pore sizing, and however the clogging of the filter is a common problem known. They are very efficient (99.9%), but not as popular due to labour costs, sanitation, and possible heat damage because of the long residence time. This system is ideal product collection and discharge system, in small batch processes. They are not recommended in the case of handling high moisture loads or hygroscopic particles.



Figure 2- 5: Schematic diagram of the spray drying system.



Figure 2- 6: Schematic illustration of different contact configuration of the spray drying process. (Masters 1991).



Figure 2- 7: Schematic diagram of spray driers (a) with external fluid bed. (b) with pneumatic conveying system. (Masters 1991)

#### 2.2.4.2 Cyclone collector

The particle separation in this unit is carried by creating a vortex of a two phase flow, from which the particles driven toward the wall of a conical draining section. The air enters tangentially at high velocity into a conical vessel, which has a much larger cross section, This velocity decreased in the cone permitting settling and sliding of solids by gravity. Higher centrifugal force can be obtained by using small diameter cyclones; several of these cyclones may be placed in parallel to reduce the losses by a range of 0.5-2%, figure (2-7). Cyclones are not as efficient (99.5%) as bag filters but several can be placed in series. In most cases a rotary airlock is used to remove powder from the cyclone.

#### 2.2.5 Spray Drying Process Characteristic and Control

Water evaporation during spray drying causes the temperature of the dry solid to be less than that of the drying air, this is known as evaporative cooling (Masters 1991). The exit air temperature is also usually much less than that of the inlet due to the heat requirement of evaporation. The process is controlled by monitoring the temperature parameters of the gas flow as function as a drying medium, because it responds readily to changes in the process and reflects the quality of the product. There are two main controls that may be used to adjust the exit air temperature (i) altering atomised feed flow rate, and (ii) altering gas inlet temperature.

The design features of the spray dryer are to meet special design specifications. The spray drying processes when designed are planned one of three different systems layout, in accordance to the cycling of the drying gas in the process.

### 2.2.5.1 Open Cycle System

This feature a single use of the drying gas followed by exhaust to the open atmosphere. Usually the exhaust gas is cleaned by passing through a cyclone, filters, and electrostatic precipitators for fine entrapments to reduce the environmental pollution. There is an energy loss however, but it may not be a concern if compared to the cost of gas dehumidification of closed cycle systems.

### 2.2.5.2 The Closed Cycle System

This system is used for the spray drying feedstock's containing organic solvents or product that are not to contact oxygen during drying, as they are of a toxic or explosive nature. This system commonly uses an inert gas, e.g. nitrogen gas, as the drying medium. These plants are gas and powder tight, and are designed to strictest safety standards. The inflammable solvent vapours produced from this system are fully recovered for disposal purposes.



Figure 2- 8: Spray drying cycles (a) open cycle, (b) closed cycle, and, (c) semi-closed cycle. www.niro.co.uk.

#### 2.2.5.3 Semi-Closed Cycle System

Semi-closed cycle system features a partial recycling gas, to ventilate and or pressure release some of the gas medium circulating in the system. This cycle application is used when there is a need for both increasing the thermal efficiency of the process and handling an active/odorous material that need to minimise its product emissions to atmosphere (Masters 1991). A version of the semi – closed system is the self-inertizing cycle. These systems are used with an inert and non toxic gas such as nitrogen, for handling products that exhibit powder explosion characteristics.

### 2.2.6 Spray Drying Advantages and Disadvantages

The advantages of spray drying is can be summarised as follow (Marshall 1954; Strumillo *et al.* 1986; Brennan 1990; Masters 1991; Coulson *et al.* 1996; Perry *et al.* 1997)

1. Formation of particulate powders from a liquid feed, cheaply.

- 2. Controlling the product quality properties by varying the atomisation and drying process parameters. These affect the product qualities such as powder density, shape, size, and temperature.
- 3. A limited capability of handling heat sensitive feeds, but these can suffer thermal degradation or loss of volatiles, and or liquids of different viscosities.
- 4. Large and continuous mass production, with minimum level of loss and use of suboperations such as filtration and sieving.
- 5. A wide drying temperatures can be used, range between 30-300°C.
- 6. Rapid Drying.

However there are some disadvantages also

- 1. The large capital cost of the industrial size dryers.
- 2. The inflexibility in term of intended use of the unit; i.e. the spray drier designed for fine processing is not suitable for drying coarse particles.
- 3. Low bulk density of the powder use, however this is can be an advantage in some cases. Non-uniform atomisation results in a particles sizing over a range of dimensions, particle size distributions.
- 4. Low thermal efficiency of drying if the drying gas exit vented to the atmosphere unless recycling systems are introduced and this results in an increase capital cost.
- 5. Problems with fines and product loss, which requires a fines recovery operation.

## 2.2.7 Spray dried products characteristics

Spray drying process is an accelerated heat and mass transfer process that keeps the product temperature well below 100°C, for food applications his ranges between 50 and 80°C. There are some draw back of product quality losses and the processing difficulties of some materials such as stickiness caused by the thermal treatment of this evaporation process. Generally the heat damage and operation conditions considered prior to processing keeping the damage to minimum. The physical properties of the products are intimately associated with the powder structure developed during spray drying that is partially controllable. Therefore the initial content and composition of the drops and their size influences the particles end quality.

Particle morphology will depend on the physical conditions under which the water is removed, where the particle may retract set or break up during the transfer pending of the gas flow, temperature, humidity and residence time of the drops (Brennan 1990; Masters 1991). The degree of processing affect on product quality is anticipated by the duration of heat exposure or residence time. This entails certain level of quality loss and deterioration of the product such as loss of volatiles, protein denaturation and structural deformation, depending on the degree of thermal processing and material composition.

# 2.2.7.1 Droplet drying

It is possible to say in spray drying most heat transfer energy is used in evaporating the mass while keeping the drop temperature constant (Masters 1991). The drop drying progress's in two steps,

- I. The constant drying rate begins, in which large proportion of evaporation occurs in a duration for the drop to decelerate from it is initial velocity to terminal velocity. The evaporation takes place on the surface controlled by vapour diffusion through a surrounding air film. The primary driving force is the temperature gradient between the two phases, gas and solidified drop (Marshall 1954; Mani *et al.* 2002). In this rate reported the formation of a skin casing covering the entire drop surface developed from the precipitation of the solute on the surface. The nature of the surface smoothness and colour is dependent on the temperature gradient within the process (Walton *et al.* 1999a).
- II. The falling drying rate which that endures high heat and mass transfer, while the particle moves in the chamber under their own gravitational force (Coulson *et al.* 1996).

The general view of the spray drying process as a non-invasive, and is not possible to measure the extent of the heat and mass transfer within the chamber. However, it is possible theorise a single drop drying profile in there periods

 The initial period of drying, release of the drop, its temperature increases to the wet bulb temperature.

- Thence a concentration gradient builds up in the drop and water activity at the surface decreases causing the surface temperature to rise above the wet bulb temperature.
- Finally internal diffusion becomes limiting. The critical moisture content is eventually reached below which the surface becomes impenetrable, leading to a developing of a hollow cased dried particle. This expansion of vapour within the impermeable hardened casing may lead to rupturing and or collapsed shell spheroid particle shaping (Masters 1991; Walton *et al.* 1999a).

The drying time is proportional to the square of the radius thus, for larger droplets the drying time may become so long that the droplet reaches the wall of the dryer while still wet. This requires the assurance of uniform spray of narrow size distribution during atomisation, leading to close mass transfer mean diameter  $D_{32}$  known as "sauter mean diameter" to the average mean diameter of the spray. Hence achieving successful drying, in almost close time of all drops in a good temperature controlled drying process.

# 2.2.7.2 Powder structure and quality and effect of production conditions

It is qualitatively and economically beneficial to have the spray-dried materials in a preconcentrated liquid form, as the evaporation from a concentrated liquid is less expensive when removing less water. Spray drying results in a different forms of hollow structured particles varying in the surface appearance and integrity, smooth or shrivelled, blistered or collapsed spheroid, ruptured or full closed particles depending on the material composition and thermal treatment severity (Masters 1991; Walton *et al.* 1999a). For example pure lactose dries into spherical particles with no dents or folds where as skim milk caseinate and other proteins always give rise to surface folds. This is explained by the uneven shrinkages of the proteins during drying unlike sugars (Fox; 1992; Roos 2000).

The compositional factor affecting the particulate physical properties during drying by developing the stickiness and cohesiveness as the water evaporates and the solute concentration increase leading to a altering the physical properties, the glass transition temperature change from that of water containing entity to that of syrup like material reaching to the amorphous state (non-crystalline) as in the case of sugar presence. Sugars rich liquids

do not crystallize during drying, it is rather forms an amorphous state, state of disarray. It is a very hygroscopic and readily absorbs moisture and eventually re-crystallise, and this is causes stickiness during drying and caking storage for many powders (Bhandari *et al.* 1997; Roos 2000; Mani *et al.* 2002).

Dried powders are categorized in two groups sticky and non-sticky products. Powder stickiness is concern in the process operation and design of the spray drying, some of these problems related to particle quality and others to the processing capability of the particles such as stickiness on the drier wall, hence losses and operational problems. Wet and plastic appearance of the particulate, that may results in a agglomeration and clumping in packing container and may be some operational problems (Roos *et al.* 1993; Bhandari *et al.* 1999; Rennie *et al.* 1999; Roos 2000; Mani *et al.* 2002).

The products that exhibits stickiness during drying are those with a sugar content or materials with a low  $T_g$  values in particular sugars and sugar rich liquids or organic acids, such as fruit juices and sugar rich foods (molasses, honey, maltodextrin), whey (acid or sweet) and high fat foods (whole milk powder is more cohesive than skim milk). The major factors causing stickiness of the dried powders are

- High hygroscopicity
- High solubility
- Low melting point temperature
- Low glass transition temperature (related to thermo-plasticity)

There are guidelines recommended for spray drying operation to avoid the complication of the stickiness, of these

- Drying below the glass transition temperature, which is not feasible.
- Mild drying temperature conditions.
- Increasing the  $T_g$  by adding high molecular weight materials, such as maltodextrins.

- Immediate cooling of the product below its  $T_g$ .
- Appropriate drier design to suit the sticky product.

The milk or other dairy products spray drying operations (whey protein) the stickiness can be caused by the presence of lactose, it has a high  $T_g$  value as indicated in table 2 that's makes it more likely to plasticize when the droplet concentrated from evaporation and the drop temperature raised toward the material  $T_g$  temperature and causing stickiness. The presence of acidic content, such as lactic acid of whey, makes the powder characteristically hygroscopic manifesting powder caking during the storage as a result of humidity and moisture adsorption. The acid presence also lowers the  $T_g$  value of whey; hence create stickiness complication during drying.

Food M	$T_g$ (°C)	
Fructose		14
Glucose		31
Galactose		32
Sucrose		62
Maltose		87
Lactose		101
Citric ac	6	
Tartric acid		18
Maltic acid		-21
Lactic Acid		-60
Maltode	xtrins	
	DE 36 (MW=550)	100
	DE 25 (MW=720)	121
	DE 20 (MW=900)	141
	DE 10 (MW=1800)	160
	DE 5 (MW=3600)	188
Starch		243

<b>Fable 2-1:</b> Glass transition temperatures	s of some food materia	lls (Bhandari <i>et al.</i> 1999)
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The surface moisture content of the powder is an important factor influence the cohesion of the particles and thence caking and stickiness of the particles with further increase in the moisture content. The reducing the particle size increases the cohesion of the particle hygroscopicity and the amorphous rubbery form of stickiness the cohesion of powder (Bhandari *et al.*), specifically in the dairy powder that is caused by the fat content. The increase in temperature during processing and or storage causes a liquefaction of the fat content of the particulate material and in result increase in cohesion of the particulate.



Figure 2-9: The mechanism of particles cohesion (Bhandari et al. 1999).

#### 2.2.7.2.1 Spray drying of biological material

Protein stability during drying determined by the retention of low level of denaturation measured in the end product (Resmini *et al.* 1989; Fox 1992). The design of protein containing powder productions must take into account the need to maintain higher order molecular structure stability of the biological material in addition to the conventional requirements of controlling inter-particle interactions and optimisation of production/handling properties (Masters 1991; Forbes *et al.* 2000). Protein denaturation measure is an extensive tool used for assessing the product quality in industrial of dairy spray drying. Thermal processing of protein containing materials induce molecular interaction and structural changes depending on the free reactive groups and amino-acids present in the protein molecule (Fox 1992). The changes to this reactant will dictate the alteration in the functional property of the protein pending on the degree of the activation induced by thermal processing. For example

the unfolding structural change due to thermal treatment alters the globular structure of the whey protein during milk product drying exposing the reactive thiol groups to and increase the hydrophobicity, hence insolubility of the whey proteins, (Kuramoto *et al.* 1959; Masters 1991; Fox 1992).

# 2.2.7.2.2 Spray drying of volatile materials – Coffee spray drying

The drying of aromatic materials in spray drying reports a volatile loss mainly due to the molecular vapour pressure of the aromatic components. The large proportion of the volatiles loss reported in atomisation zone (King 1982). There are several mechanisms reported explaining the loss of volatiles (Coumans *et al.* 1994)

- Losses during atomisation from the sheeted liquid during atomisation from a pressure nozzle.
- Losses from the formed droplets and the internal motion preventing the formation of the dry skin, hence loss from liquid by diffusion.
- Bad gas motion surrounding the drops in the spraying zone of a dense spray,
- And finally during drying losses due to morphological changes and diffusional transfer from the drop.

The common example on volatile losses in spray dried is signified coffee aroma loss from the spray dried coffee powder, in typical industrial process the powder is aromatised prior to packaging (Johonson *et al.* 1974; Desrosier *et al.* 1979).

## 2.2.7.2.3 Spray drying powder hydration

Many spray-dried powders do not disperse readily in water. The difficulties are associated with the exterior of the powder absorbing water very rapidly and forming lumps, dry on the inside but covered with a viscous layer through which water penetrates very slowly (Masters 1991; Lillford *et al.* 1998). The problem arises particularly in products, which contain soluble proteins, such as milk powder and flour. The requirements for rapid dispersibility of powders in cold water suggested that the powders are (i) a large wet able surface, (ii) sink ability (must not float on surface), (iii) solubility, and (vi) resistance to sedimentation.

The wet ability is crucial and depends upon the total surface area of the powder, as well as the surface property such as porosity of the particle. In spray drying water is evaporated of the surface of the drop in the constant rate of evaporation and thence rapidly and forms a crust on the surface, this crust traps the vapour inside the particle. The continuous evaporation will lead to diffusion of the vapour if possible leaving a hollow particle or ruptures the crust surface to vent the vapour. If the surface of the particle is porous water passage to the centre of the particle is eased, thence porosity enhances wetting and solubility of the powders. The spray drying industry in had improved dispersibility characteristics of the products by a combination of surface treatments (for example addition of lecithin) and 'instantizing' (agglomeration). Instantizing is an aggregation process, which is intended to prevent powder particles from sticking together and becoming lumpy during rehydration (Masters 1991; Lillford *et al.* 1998; Walton *et al.* 1999b).

### 2.2.7.2.4 Spray drying process modelling

The drying rate is a function of the temperature and humidity of the drying gas, the droplet mean diameter and the nature of solute constituent in the drop, and the relative velocity of the drop to the gas stream travelling through. For a conical spray the drops released in a conical movement pattern with a possible swirling motion, which give it a three axial motion projectile. The heat and mass transfer of evaporation in the spray drying described by the exchange of "a single drop settling in a gas flow" (Gauvin *et al.* 1976; Miura *et al.* 1980; Masters 1991; Coulson *et al.* 1996). The all the models represented in a similar analogy, but the differ in the velocity projectile in the spray. There are different velocity components can be determined for the droplet in the spray (axial  $[v_a]$ , tangential  $[v_t]$  and radial  $[v_r]$  velocities), depending on the investigator measurement of the drop velocity profiling the spray drying can be modelled in a unidirectional (Masters 1991), two directional (Miura *et al.* 1980), and 3 directional (Gauvin *et al.* 1976).

#### **Droplet trajectory**

The three dimensional equation of the drop motion a centrifugal field can be written as

$$\frac{dv_{v}}{dt} = g - \frac{3C_{D}\rho_{g}v_{f}(v_{v} - v_{gv})}{4d_{i}\rho}$$
 Eq (2-1)

$$v_f^2 = (v_t - v_{gt})^2 + (v_v - v_{gv})^2 - (v_r - v_{gr})^2$$
 Eq (2-2)

The drag coefficient ( $C_D$ ) determined from different mathematical correlation for a particle moving in gaseous stream, but for the purpose of simplicity preference the equation set by White (1974) is recommended and it is suitable for a range of droplet Reynolds no. (0-2.0x105) (Kladas *et al.* 1993).

$$C_D = 0.4 + \left(\frac{24}{\text{Re}_d}\right) + \frac{6}{1 + \sqrt{\text{Re}_d}}$$
 Eq (2-3)

Where  $Re_d$  is the Reynolds number of the droplet/particle.

The drag force  $(F_D)$  acting on the droplet can be determined from the

$$F_{D} = 20.25 \rho_{g} d_{i}^{2} \left(\frac{v_{g}}{K}\right)^{0.5} K v_{f}$$
 Eq (2-5)

$$K = 1.4\nu_{gv} \left(\frac{r}{r_5^2}\right)$$
 Eq (2-6)

These motion of droplet equations are solved simultaneously with the heat and mass transfer equations to include the air flow thermal property.

#### **Droplet evaporation**

The droplet heat  $(dq_i/dt_i)$  and mass  $(dm_i/dt_i)$  transfer determined from heat and mass balance equations of drops/particle

$$\frac{dq_i}{dt_i} = \pi k_g N u \ d_i \ n_i (t_g - t_s)$$
 Eq (2-7)

$$\frac{dm_i}{dt_i} = \pi D_g \rho_g Sh d_i n_i (H_w - H)$$
 Eq (2-8)

The Nusselt no. (Nu) and Sherwood no. (Sh) are dimensionless number specific to the nature of the two phase heat transfer and flow dynamics, for a spherical drop in gas flow these are equal to

$$Sh = 2.0 + 0.6 \,\mathrm{Re}^{0.5} \,Sc^{0.33}$$
 Eq (2-10)

Prandtl number (Pr) is a dimensionless number represent the ration of moment and thermal diffusivity. Schmidt number (Sc) is the dimensionless number characterises the relation of gas viscosity and diffusion to it self in convective heat transfer (Hall 1992).

$$Sc = \frac{\mu_g}{\rho_g D_g}$$
 Eq (2-12)

$$H_{w} = \frac{18p_{w}}{29(p_{t} - p_{w})}$$
 Eq (2-13)

Where	8	=	Acceleration due to gravity (9.81 ms <sup>-2</sup> )
	$ ho_{g}$	=	Gas density (kg m <sup>-3</sup> )
ρ		=	droplet density (kg m <sup>-3</sup> )
	$v_f$	=	Resultant drop relative velocity to gas flow (ms <sup>-1</sup> )
	v <sub>gv</sub> , v <sub>gt,</sub> v <sub>gr</sub>	=	Gas axial, tangential and radial velocities respectively (ms <sup>-1</sup> )
d <sub>i</sub> K r		=	Droplet diameter of each class size of a spray ( $\mu$ m).
		=	The curl of fluid velocity (s <sup>-1</sup> )
		=	Radial position of the drop (m)
	<b>r</b> 5	=	Velocity half radius (m)
$k_g$		=	Drying gas thermal conductivity (J ms <sup>-1</sup> K <sup>-1</sup> )
	t <sub>g</sub> , t <sub>s</sub>	=	The temperature of the drying gas and droplet surface respectively (K)
$H_{w}$ , $H$		=	Saturation humidity and absolute humidity respectively
			(kg <sub>water vapour</sub> /kg <sub>of dry gas</sub> )
	$C_{pg}$	=	The gas specific heat capacity (Jkg <sup>-1</sup> K <sup>-1</sup> )
	Dg	=	Gas diffusivity (m <sup>2</sup> s <sup>-1</sup> )
	$p_{t}$	=	Total pressure in the spray drying chamber (Pa)
	$p_w$	=	Vapour pressure at the droplet surface (Pa).

#### 2.3 Fluidised Bed Drying

Fluidisation drying is an attractive evaporative process for particles inducing a high heat and mass transfer of a large dried particulate surface area in a relatively small space and predetermined time duration. The technique has been used industrially since 1948 in wide spread industries of food, pharmaceutical, crystalline materials and many others (Geldart 1986). The fluidisation operation employed in range two phase contact of solid to gas contact processes due to the intimate contacts of the two phase and achievement of high heat and mass transfer coefficient (Kunii *et al.* 1991; Coulson *et al.* 1996; Perry *et al.* 1997).

The fluidised bed drier composed of a fluidisation vessel or container, gas distributor, a dried bulk and source of drying gas, and fine reclaiming unit (cyclone or filter bags), see figure (2-10). Fluidisation is a process of suspending a bulk of solid particles in an up flowing current of gas or liquid stream, where the particles assume a fluid like behaviour. Consider a bed of spherical solid particles (uniform shape and size) in a vessel subjected to an upward moving gas stream. The particles in the bed, starting from diagram (A) in figure (2-10), at low fluidisation gas velocity remains in packed bed. As the gas flow is increased this bed becomes loosely packed at low fluid stream velocity (B) this fluid velocity is known as the minimum fluidisation velocity  $U_{mf}$ . Further increase in the fluidisation gas velocity to an intermediate level results in the formation of boiling action of the particles in the bed (C) which is aggregated to become slugging bed when this velocity increased further (D). The diluted phase is the case bed particulate becomes a homogeneous bulk with a uniform spatial arrangement within the vessel (E), here the velocity has reached a level just below the terminal velocity of the particles  $U_t$ . Beyond this fluidisation gas velocity the particle will be carried over out of the system, where the buoyancy and drag forces on the particulate are higher than the gravity force on the particle (Geldart 1986; Strumillo et al. 1986; Kunii et al. 1991).

In fluidised bed drying the drying medium, usually dry air or inert gas, will surround the particulates, which create forced convection heat and mass transfer. This transfers the moisture or the solvent by diffusion through the boundary layer of the drying gas from the particulate surface. The mass transfer process accelerated by the constant breaking of

boundary layer due to particle-particle collisions. The evaporation or sublimation of the water in this process exists as a result of the temperature and vapour pressure gradient between the two mediums, which acts as the heat and mass transfer driving forces respectively (Vanecek *et al.* 1966).



Figure 2-10: Schematic diagram of the fluidised bed drier.



Figure 2- 11: Schematic diagram of fluidisation types obtained at different fluid velocities, (a) particulate bed, dense phase, (b) boiling bed, (c) bubbling bed, (d) slugging bed, and (e) diluted phase.

### 2.3.1 Fluidised bed design

Fluidised bed drying has been successfully used in drying operations in the food, pharmaceutical and chemical industries in both batch and continuous setups (Geldart 1986; Wolff *et al.* 1990; Kunii *et al.* 1991). The main difference between these is the material feeder and product collector. The drying gas is blown into the drying vessel through a mesh or a

sintered grid in an upward direction where the material fluidises. Upon drying the particles become less dense and lifted up to the discharge outlet. The fluidising vessel has a disengagement space, which is large in comparison to the fluidisation space, and functions as a settling space for untreated carry over particles (Perry *et al.* 1997). The most important part of the fluidiser is the gas distributor, as it its affects the process efficiency and performance (Senadeera *et al.* 2000). The application and performance of number of fluidisation distributor types such as nozzles and meshes were explained by Kunii et al (1991) and Senadeera *et al.* (2000). Fluidised bed dryers contain other ancillary units such as discharger of the dried solids, gas moving equipment, and dust arrestor's.

There are many varieties of fluidised bed dryer design depending on the specific applications. The flexibility in the design, the variety of types materials that can be dried as well as the drying load capacity confers this drying method with great interest to engineers. For example it is possible to construct a fluidised bed drier with different temperature zones, termed "multi stage drier". Also fluidisation drying can be applied as continuation to a previous drying operation (spray drier with integrated fluidised bed) (Masters 1991). Much work is available in the literature concerning the design and operation fluidised beds drying, but all agree that designing a fluidisation processing unit is usually a matter of trail and error (Vanecek *et al.* 1966; Kunii *et al.* 1991). Similar to spray drying there are no universal and simple prediction methods of the process. As the rate of heat and mass transfers depend on the processed material thermo-physical and dynamical properties, which in turn vary with time throughout the operation.

The main limitation of the fluidised bed drying is the capability of handling of fluidisable materials (particulate) only. Materials that are too wet to fluidise usually agglomerate due to the high moisture contact on the surface. The limitation is the size distribution requirement of small and narrow distribution, as the providing high velocity to fluidise the large particles may result in loss of small sizes of the range. However these limitations are possible to over come by flash thermal processing of the material if they are too wet , and using vibrating fluidisation for materials of wide distribution in sizing. But to this extent these solutions are specific to certain materials that may results in process efficiency or product quality reduction (Geldart 1986).

A broad characterisation of the particulate behaviour was made by Geldart focused on the material parameters characteristic for fluidisation of particles and classified them into groups. Figure (2-11) shows these groups in a logarithmic representation of the particles buoyancy in relation to the particulate size or diameter (Geldart 1986; Kunii *et al.* 1991).



Figure 2- 12: Geldart classification of fluidize-able particles at atmospheric conditions. (Kunii et al. 1991).

Group (A): Fine aeratable particles usually finer light. Easily fluidized at low fluidization velocities.

- **Group (B):** Sand like particles, more common and the easiest to manipulate, the particles diameters  $40 < d_p < 500 \ \mu m$  and density  $1400 < \rho_p < 4000 \ \text{kgm}^{-3}$ .
- Group (C): Fine cohesive powder, hard to fluidize.
- Group (D): Spoutable large and dense particles. Care must be exercised if one uses correlations to calculate their fluidization properties.

## 2.3.2 Advantages and Disadvantages of Fluidised bed Drying

The advantages of drying by fluidisation is summarised in the following list

- 1. Low capital cost of construction.
- 2. High rates of heat and mass transfer as result of forced convection, mixing and inter particle collision.
- 3. Good drying times for particulate, which exhibits mostly constant rate (surface) drying.

- 4. The ability to operate in a batch and continuous modes.
- 5. Process flexibility to be used as an ancillary unit of other processes, for example agglomerate attached to the spray drier.
- 6. Controlled thermal treatment of heat sensitive materials, i.e. low temperature or vacuum fluidisation.
- 7. Easy maintenance and easy management of the operation.

However there are some disadvantages to this process such as

- 1. Large residence time for products with a prolonged falling rate of drying, which may result in partial drying of some particulate.
- 2. The process is suitable for easily fluidised particles only.
- 3. During drying the change in the particulate property (such as density) may require a change in the fluidisation velocity. The change in the particle mass with drying may result in carry over the particles if the fluidisation velocity remains constant.
- 4. From a design and construction point of view there are few theoretical models for the operational and constructional conditions of the fluidisation process. The design is mainly reliant on empirical and experimentation findings.

# 2.3.3 Vacuum and low pressure fluidisation

The sublimation by fluidisation was reported by a number of researchers in a different format of design and research interests. The latest was the research by Mumenthaler et al. (1991); he reported that ice sublimation in atmospheric pressure lasted for number of hours. Therefore low pressure For the purpose of process acceleration the use of partial vacuum suggested as possible option of operation in this research. Vacuum fluidisation suggested by Llop et al (1996) as refining drying procedure to thermally delicate fine particulate. Kozanoglu et al (2001) stated that vacuum fluidised bed drying is a viable approach for dehydrating the thermo labile pharmaceutical materials. Although a relatively small number of literature are available in vacuum fluidisation application and research.

Kawamura and Imada (1980) had reported that as far as there is a viscous gas flow region in a fluidised bed under a low pressure operations the fluidizing characteristics are maintained in the same manner as under atmospheric pressure (Kawamura et al. 1980; Kozanoglu et al. 2002). Germain and Claudel (1976) had experiment the fluidisation of a glass balls with nitrogen flow at pressure t mean pressures between 500 to 40000 Pa. Low pressure fluidisation have a laminar flow regime which is different from that of the atmospheric system, however the hydrodynamic behaviour of fluidised particles shows bubbling and onset fluidisation is similar to that of the atmospheric pressure, fluidisation increases with gas flow rate increase. The difference on the other hand is in the minimal fluidisation velocity relation with pressure. Pressure reduction increases the minimum fluidisations in this case the conventional fluidisation equations of are not applicable. Group A and B particulate material are shown to be fluidised smoothly under vacuum in a shallow bed at pressure range of 0.1 to 1 bar, and the flow regime is in the slip flow region (Kozanoglu et al. 2001). Hence the flow in question is a function of the Knudsen number, which is a ration of the mean free path to the diameter of the particle. A generalised minimum fluidisation  $U_{mf}$  velocity equation suitable for low pressure fluidisation in the slip flow region pending on the sphericity of the particles (Llop et al. 1996)

For particle sphericity ( $\phi > 0.80$ )

$$\operatorname{Re}_{mf} = \left[ \left( \frac{0.909}{K_{n_p} + 0.0309} \right)^2 + 0.0357 Ar \right]^{(1/2)} - \left( \frac{0.909}{K_{n_p} + 0.0309} \right) \qquad \text{Eq (2-14)}$$

For particle sphericity ( $0.5 < \phi \le 0.80$ )

$$\operatorname{Re}_{nf} = \left[ \left( \frac{1.9}{K_{n_p} + 0.0492} \right)^2 + 0.0571 Ar \right]^{(1/2)} - \left( \frac{1.9}{K_{n_p} + 0.0492} \right) \qquad \operatorname{Eq} (2-15)$$

Where  $Re_{mf}$  = Reynolds number of the minimum fluidisation value =  $\frac{U_{mf} \rho_s D_p}{\mu}$ 

Ar = Archimedes number = 
$$\frac{d_p^3 \rho_g (\rho_p - \rho_g)g}{\mu_g^2}$$

K <sub>np</sub>	= Knudsen number of a particle = $\frac{\overline{\sigma}}{d_p}$
σ	= mean free path
$D_p$	= particle diameter
$ ho_p$	= particle density respectively
μ	= gas viscosity

The mass transfer of a particulate material in fluidised bed defined to be a subject of vapour diffusion, first from the dry layer then through the boundary film on the surface, therefore vapour diffusion in fluidisation is affected by the operating pressure condition. Yamamoto and Kawamura (1980) reported that fluidisation under reduced pressure would have no significant effect on the heat transfer while the mass transfer increases sufficiently (Yamamoto *et al.* 1980). The formulated the mass transfer relation in the vacuum fluidised bed drier of the slip flow regime as function of the pressure in a dimensionless Sherwood number (*Sh*), and found the mass transfer increase exponentially as the pressure decreases (Kozanoglu *et al.* 2002).

$$Sh = 5882 \operatorname{Re}_{p}^{3.07} K_{n_{p}}^{2.94}$$
 Eq (2-16)

Where  $Re_p$  = particle Reynolds number

## 2.3.4 Dried particulate characteristics

The particulate dried in the fluidised bed drier are solid in nature containing a level of moisture. The evaporation of this solid particulate will leave characteristically a shrivelled or wrinkled full solid.

# 2.4 Freeze - Drying

Most evaporative dehydration processes confer characteristic storage stability to the dried product either for distribution and or other application purposes, but it is often inflicts some end product quality losses. Freeze-drying is a sublimation dehydration process, which operates at low temperature, and as a result losses in product quality, loss of volatiles, shrinkage, or other quality degradation features are very much reduced. Freeze-drying is also known as Lyophilization (Lyophilized is a Greek derived word which means "made solvent-loving" this a consequence of the porous structure which allows easy rehydration), is an expensive form of drying that its use usually restricted to delicate, heat-sensitive and high value materials.

# 2.4.1 Lyophilization Process Overview

Thomas Jennings originally defined the lyophilization process as follow;" It is a *stabilising process* in which a substance is first *frozen* and then the quantity of the solvent (generally water) is *reduced*, first by *sublimation* (referred to as the primary drying process) and then *dsorption* (known as the secondary drying process) to values that will no longer support biological activity or chemical reactions (Jennings 1999). These three key stages of the above definition will now be looked at in turn.

# 2.4.1.1 Freezing

Freeze drying process initially stabilises the material by slowing the kinetic changes related to either biological activity or chemical reactions by holding the material within a rigid matrix, frozen state. Successful freeze-drying requires the material to be frozen to temperature below the eutectic melting point (if crystalline) and keeping any amorphous regions below their glass transition temperature. Knowing this depends on the solution formulation, the solid contents and type of the material (Roos *et al.* 1991). During freezing of aqueous solutions separates into two phases in an interstitial structure the freezing, ice is formed as pure water goes through the two-step (nucleation and propagation) crystallisation process. An aqueous solution freezes in different temperatures depending on the solute content and type of the constituents. Ice formation is an important phenomena leading to sublimation, if there is no ice formation there is no freeze-drying. Interstitial region formation of a solution for a non-rapid process produces relatively large ice crystals, the matter formulation will change the

concentration with time. Thus for the most part the ice that is formed is relatively pure and the resulting concentrated solution is confined between the ice crystals. This concentration increase will decrease the temperature of the freezing solution. So the combination of these two changes may lead to a variety of results and thoughts. However not all water is separated and solidifies, some are remain bound to the interstitial solute. Thence solute type and concentration in a solution is an effecting factor in the matrix formation and it necessary to determine the freezing temperature, and identifying the primary drying temperature of the freeze-drying (Mellor 1978; Jennings 1999).

Thence freezing is a phase transition process leading to a product with low moisture content containing a non-crystalline existed in either solid (glassy state) or supercooled (rubbers state). The latter is leads to collapse of drying materials, the extent of collapse and the rate of crystallisation is dependent moisture content and the solute nature (Roos *et al.* 1993).

## 2.4.1.1.1 Glassy State

It is a state of excess entropy, caused by a state of disorder in the interstitial frozen matrix. It is a typical of organic and inorganic materials such as food components, sugar and proteins. This state is different for the same solution and its prediction remains illusive, as it is changing over a range of temperatures, though it is usually determined from extrapolation of a melting curve of the sample frozen state (Reid *et al.* 1993; Jennings 1999). The glass transition temperature ( $T_g$ ) range is dependent on the molecular weight of the components, materials such as sugars have a clear glass transition temperature, see table (2-1), whereas high molecular weight such as proteins have a wide range and it is more difficult to determine temperature (Roos *et al.* 1993; Roos 2000).

## 2.4.1.1.2 Eutectic Mixture

It is a region of forming an interstitial structure, known to be a sharp and well defined melting of the interstitial region, though it is rarely detect (if not never) (Jennings 1999). The eutectic mixture concluded by the sudden melting of the ice to liquid. The achievement of a true eutectic mixture in freeze-drying formulation is advantageous to maintain a defined and easily detected phase change values. From the process validation point an eutectic mixture in the interstitial region preferred over a glassy transition, but it was not easily achieved.

### 2.4.1.1.3 Freezing process of Crystallisation

Consider freezing of pure water and of a sucrose/water solution. The time temperature profiles indicated in figure (2-12) show a difference in the freezing time and temperature, but both profiles are relatively have same trend. The curves can be interpreted as follows:

- AB: represents the solution cooling from its initial temperature to it nonequilibrium meta-stable state at which ice nucleation begins. Though, pure water can be under cooled by several degrees before the nucleation phenomenon begins, in some cases may reach -40 °C without nucleation. However, solute presence in aqueous solutions such as salts, sugars, microrganisms, etc. can acts as nucleation agents and promotes heterogeneous nucleation and this will raise the nucleation temperature significantly (Liao *et al.* 1990; Hindmarsh *et al.* 2003).
- BC: represents the latent heat of fusion release, after the onset of crystallisation. The temperature increases instantly to the initial freezing temperature,  $T_f$ , of the solution at Point C or C'. Solutes present will depress the freezing point temperature.
- **CD**: is the main phase change regime for pure water, it reflects the time during which crystal growth occurs. This line is almost linear, and the sub-freeze-cooling or tempering will not occur until all freeze-able water is solidified. In solutions this portion is reduced hence depending on the solute content the duration of this phase change stage in freezing is shortened. Aqueous solution freezing witness a freeze-concentration process, which occurs as water freezes out of solution in the form of pure ice crystals C'D'. This concentration increase of the solutes causes further freezing point depression until it reaches a high viscosity level that hinders the diffusion processes and effectively ceases crystallisation.
- **DE:** is the tempering or sub-freeze-cooling line, in which the product reach's the storage temperature.



Figure 2-13: Freezing profile of pure water and sugar solution (picture taken from <u>www.foodsci.uoguelph.ca</u>).



Figure 2- 14: State diagram of Sucrose solution showing the experimental data of (Roos 1997).

A recent study by Hindmarsh et al (2003) had reported similar sequence of freezing stages determined experimentally for single water drop suspended on thermocouple, freezing process is composed of a number of stages: (i) initial cooling to a supercooled temperature, (ii) nucleation, (iii) decalescence, whereby rapid crystal growth occurs at the expense of sensible heat from the supercooled droplet, and (iv) further, slower crystal growth which is limited by heat transfer from the gas.

#### 2.4.1.1.4 Freezing in freeze-drying

Ice crystals formation occurs if the freezing temperature sufficiently low to allow maximum ice formation according to the equilibrium melting temperature curve, figure 11, ice formation occurs in the temperature range of  $T'_g$  to  $T'_m$  (Roos 1997). The microstructure, size and shape of these ice crystals depend on the rate of freezing. Rapid freezing operations produces uniform and homogeneous ice crystals, which is important in freeze drying process that boosts the mass transfer rate during sublimation, as well as the structure and quality of the final dry products by having a uniformly porous matrix, Quast & Karel, 1975 (MacCarthy *et al.* 1986; Mumenthaler *et al.* 1991; McGrath *et al.* 1992; Hampden-Smith *et al.* 1999; Jennings 1999).

The main objective of freezing (phase change) is locking the mobile water of a material in an interstitial matrix of pure ice crystals and a concentrated or solid phase, containing residual water. Upon freezing the free water crystallises and the viscosity of the freezing material increases gradually till it reaches the *glassy* or *vitreous* state, and the matrix viscosity reaches  $10^{10}$  to  $10^{14}$  Pa.s. The interstitial region formed during freezing for most formulations consist of a glassy state, which is a highly disordered state and excess entropy in a frozen material (Roos *et al.* 1991; Roos 1997; Strumillo *et al.* 1998). The viscosity exponential increase effects the phase diffusion on mass transfer properties acts as the limiting factor on the ice crystal growth. Glassy state is not stochiometic and time dependent in nature, i.e. if freezing were repeated for the same solution numerous times the glassy state would be different with each freezing (Brennan 1990). In freeze-drying this variation in glassy state temperature  $T_g$  can have a serious impact on both the freezing and primary drying processes. The glassy transition temperature can be calculated from Gordon and Taylor (1952) equation (Roos 1997).

$$T_{g} = \frac{w_{1}T_{g1} + kw_{2}T_{g2}}{w_{1} + kw_{2}}$$
 Eq (2-17)

Where $T_{g2}$ = glass transition temperature of component 1 (Sucrose 335 K). $T_{g2}$ = glass transition temperature of component 2 (Water 138 K). $w_{1\&2}$ = mass fraction of component 1 and 2.K= constant (4.7 ± 0.2 for water sucrose solution).

The state diagram characterises the amorphous physical state relation to the solute concentration in biological material, i.e. predict the amount of ice at any given temperature, which is a function of freezing point depression and hence the number of solutes fraction. However it doesn't predict anything about ice crystal size.

The formulations of freeze-dried material had what is referred to as a collapse temperature and is defined as that temperature at which the mobility of the water in the interstitial region becomes significant (Roos *et al.* 1993; Jennings 1999). It is the process engineering parameter of prime importance and derived from the  $T_g$  and  $T_{eutectic}$  depending on the system. The collapse temperatures were generally found not to be sharp and well defined because it represents a measure of the onset temperature for melting of a glassy state, it varies depending on the nature of the solutes in the original solution, formulation of the freeze-dried material. The fact is not all the water is freeze-able, but also un-complete freezing process or recrystallisation may lead to collapsing of the dried material in freeze-drying. Collapse is a faulty case of freeze-drying in which the structure of the frozen material is lost due to water is removed by evaporation rather than sublimation. This in turn compromises the highly porous texture of freeze-dried material with a shrunk collapsed matter, hence it is undesired feature and most attention is directed to it prevention.



Figure 2-15: Collapse demonstration in freeze-drying (Roos 1997).

From figure (2-14) the sublimation temperature should be lower than the ice melting temperature  $T'_m$ , to allow a successful dehydration without collapse. The reasons for collapsing during the freeze-drying referred to one or more of theses reasons;

- In freeze-drying the frozen layer has a higher than  $T'_m$ , due to the plasticization of the freeze-concentrated solute, which makes the material un able to support its weight then collapses.
- Also the successful freeze-dried material may collapse if stored at temperatures higher than  $T_g$  of the material
- Or due to water sorption and plasticization which depresses the  $T_g$  of the material.

## 2.4.1.2 Primary Drying – Sublimation

Sublimation is the process of converting a substance directly from the solid phase into the vapour without passing through an intermediate liquid phase. Natural sublimation occurs at temperature and vapour pressure below the triple point, but the vapour pressure should be below the equilibrium vapour pressure line, otherwise the reverse process of vapour condensation will take place instead, see figure (2-15) (Goldblith *et al.* 1975; Mellor 1978; Jennings 1999; Oetjen 1999). Sublimation of the ice leaves voids in the material structure that makes it characteristically porous. Water vapour diffuses through this porous layer to the surface of the. Primary drying refers to the phase of freeze-drying when ice crystals are subliming, however, a significant quantity of water is still present in the concentrated phase after the primary drying phase has completed.



Figure 2-16: The Phase Diagram of Water (Oetjen 1999).

Sublimation in freeze-drying is slowed by the presence of gases on the frozen material surface as they create mass transfer resistance, according to their diffusion capacitance (Flosdorf 1949; Mellor 1978; Boeh-Ocansey *et al.* 1986). Therefore decreasing the gas phase pressure surrounding the dried surface would increase the rate vapour diffusion through the gaseous surround, hence the drying process is accelerated, this can be accomplished by placing the frozen material in a vacuum vessel. On the iced material side vacuum suction helps driving vapour molecules through the solidified and dried surfaces and out into the drying space of the vessel.



Figure 2- 17: Water vapour volume as a function of partial water vapour pressure. Temperature indicated on the plot is of the ice (Oetjen 1999)

The heat transfer associated with this mass diffusion of water vapour is an intake of the latent heat of sublimation from the surroundings into the dried material, this latent heat is equivalent of 3 kJ to sublimate one gram of ice. This heat intake reduces the material temperature as in result and therefore should be compensated, to prevent the slow down in mass transfer as a result of the lowering of the vapour pressure driving force. thence heat of sublimation input into the system of freeze-drying reverse the declining rate of mass transfer. In the current designs of the freeze-drying vessels this heat of sublimation is provided mainly by radiation, and or conduction to the dried material.

#### 2.4.1.3 Secondary Drying – Dsorption

At the end of sublimation stage and the removal of the frozen solvent, we can recognise the product as partially dried (Jennings 1999). However, some bound water still remains within matrix of the material, typically consisting of 5% (w/w) of this concentrate. For an acceptable stabilisation level or drying or the processed material a portion of this moisture must be removed in the dsorption stage, and this is known as secondary drying. Some products require *An Investigation of Spray-freezing & Spray-Freeze-Drying* 43

that the moisture content does not exceed 1% with no lower limit. However, there are products, e.g. proteins and hydrates that may require an upper and lower moisture limit in order to achieve product stability. Secondary drying can be accomplished at higher temperature than primary drying without deteriorating the product quality as the moisture content is low, and this will increase the drying rate.

#### 2.4.2 Spray freezing

It was established that spraying operations are a size enhancement, control, and heat and mass transfer acceleration tool, section 2.2. There are two types of spray freezing operations cryo-spray freezing and spray freezing in cold gases.

The importance of the freezing step is almost obvious since it is the first process step, and because the characteristics of the frozen matrix determine how the rest of the process will run. The freezing of a solution starts with nucleation, the spontaneous aggregation of water molecules to form a template to which other molecules can attach and ultimately form a crystal. As the temperature drops below the equilibrium freezing point, the probability of nucleation increases, because of a thermodynamic driving force, and ultimately decreases due to kinetic limitations imposed by high viscosity. The freezing method used can have a significant effect on ice morphology, affecting both the resistance to vapour flow during primary drying and also quality of the final product when collapse is a problem (Rambhatla *et al.* 2002).

Spray freezing in cryogenic medium; it a rapid freezing operation of a spray impinged in a pool cryogenic medium (mostly liquid nitrogen). This is frequently used in most spray freezedrying of pharmaceuticals and biological studies (Chang *et al.* 1991; Fun Maa *et al.* 1999; Sonner 2002). The simplicity of process setting and operation makes it more attractive for the ceramic and supper conductor industries, see figure (2-17) (Roehrig *et al.* 1972; McGrath *et al.* 1992; Matsuda *et al.* 1993; Hampden-Smith *et al.* 1999). Freezing rate imposed in cryospray-freezing process typically more than 150 °C per unit time. However, most operation the gas space head above the freezing medium surface cools during operation, thence this is effectively spray freezing in gas stored in liquid nitrogen. This operation requires continuous stirring to reduce the risk of powder lumping in the pool of cryogen.



Figure 2-18: Cryo-spray freezing rig developed by Kimura et al 1991 (Hampden-Smith *et al.* 1999).

Spraying in cold gaseous environment; this process type is less rapidity in freezing, typically 10's of °C per unit time, thought it has a higher risk of agglomeration and snowmaking. It is commonly used in the snow making technology, spraying a liquid feed into open cold air, typically <-10 °C (Liao *et al.* 1990; Gao *et al.* 2000). It is also attracted and interest in the freeze-drying industry of pharmaceuticals by producing more porous structure than cryospray freezing. (Mumenthaler *et al.* 1991). The design of the spray-freezing rig was reported to be more sophisticated and requires a good deal temperature and environmental control, see figure (1-2).

### 2.4.3 Spray freeze-drying

The spray freeze-drying process is a controlled instantaneous spraying and freezing operations followed by duration of sublimation in controlled pressure environment. This technique may ensure high-quality particles production, and eliminating the solute migration effect by stabilising the solution in a solid matrix with interstitial ice crystals within a particle, that leaves voids after drying and good pore size distribution. The case of solute solvent separation is also tuned down in the case of spray freezing by small crystal formation result of rapid

freezing process. Freezing is a critical step in the production of structurally acceptable freezedried material. A fast cooling rate normally gives greater super-cooling, inducing a lower nucleation temperature and therefore smaller ice crystals, increasing primary drying time (Wang 2000). The particulate size control in the spray freezing process gives a reasonable degree of size homogenisation of the produced dried particulate pending on the spray nozzle type and operation pressure (Masters 1991).

The spray freeze-drying have the advantages of producing enhanced size and morphologydried product that has characteristics freeze-dried materials. In addition to this the spraying operation helps accelerating the drying rate by increasing the surface are to volume ratio.

# 2.4.4 Freeze-drying process modelling

Freeze-drying is the core drying technique of the current research and therefore modelling of freeze-drying is pertinent to this study. Freeze-drying process progresses in three successive stages, as described earlier, so the overall modelling of the process should also be studied similarly (Mellor 1978). Hence each stage is usually be modelled separately, and the freeze dried material initial parameters are considered from the initial liquid or wet condition and progresses to that of the end product characteristics of each stage that is forwarded to the next.

# 2.4.4.1 Freezing modelling

Regardless of the quantity characteristics the major reason for modelling freezing is to predict freezing times. The *freezing time* is usually defined as the time from the onset of nucleation to the end of the crystal growth phase. The calculations involves solving equations for unsteady state conduction with phase change which are difficult to perform, and hence simplified models are often used. (Brennan 1990). The crudest and the highly simplified model of freezing time prediction is the one established by Planck (1954). His mathematical model on food block freezing time prediction was based on the following assumptions (Brennan 1990; Lewis 1990);

- The freezing body has a uniform and sharp freezing temperature.
- The freezing body density and thermal conductivity are independent of temperature.
- Freezing commences while the material at the freezing temperature, i.e. latent heat only and not sensible heat is considered.
- Heat transfer from the freezing surface into the cooling medium is in steady state.
- The freezing medium has constant temperature and heat transfer coefficient.
- Constant thermal conductivity of ice.

$$t = \left(\frac{\lambda\rho}{\Delta T}\left[P\frac{r}{h} + R\frac{r^2}{2k}\right]\right]$$
 Eq (2-18)

Where

t

= time (s)

λ	= latent heat of fusion (kJ kg <sup>-1</sup> ),
$\Delta T$	= $T_{\text{freezing}} - T_{\text{coolant}}$ (K)
T <sub>freezing</sub>	= Freezing temperature of the substance (K)
$T_{coolant}$	= the freezing gas temperature (K)
P	= 1/6(for a sphere, drop)
R	= 1/24 (for a sphere, drop)
h	= heat transfer coefficient ( $Wm^{-2}k^{-1}$ )
k	= thermal conductivity $(Wm^{-1}K^{-1})$

Planck's equation gives a crude indication of the freezing time range, since it considers the phase change duration of the freezing period regardless of the pre-cooling and the tempering period which are to be added and does not include sensible heat considerations. There are many other models both analytical and numerical which have been developed more recently such as those of Singh and Heldman (1984), Cleland and Earle (1982). The most interesting is that of Pham (1984), whom achieved close approximation of the overall freezing time prediction (including the pre-cooling and tempering periods) from a modified version of Planck's equation.

Pham's idea is to assume the latent heat of freezing released at a single mean freezing temperature common to all aqueous food material which varies with final centre temperature of the material and the air temperature. He took into consideration the heat transfer resistance based on the mean conducting path of the material. The derived model is more realistic in approach to the practical application of food freezing by taking into account the sensible heat

of the material. The achievement of this modelling success is done by considering the temperature of the freezing front to be located in single point just away from the freezing front interface and material surface.

Freezing heat transfer modelling is commonly based on Newton's law of cooling, by defining the heat transfer coefficient to count for the actual heat transfer mechanism. The conduction heat transfer resistance of the solidified layer, or the solid content of freezing material, would not be accounted for, due to the difficulties of accurately predicting the thermal conductivity changes using analytical method based on the temperature changes, which is best predicted by a numerical method (Pham 1984). According to this model the complete freezing process is sub-divided into

- 1. An initial cooling period, where the material temperature drops down to the freezing point temperature.
- 2. The phase change period occurs at the freezing mean temperature of the material (1.5 degree below the freezing point).
- 3. Finally the sub-cooling period, here the material temperature continues to drop down until it reaches the storage freezing temperature.

Based on Newton's law of cooling, Pham had considered the boundary condition of the system are of the third kind where the heat flux at the surface is proportional to the temperature difference with the environment. The major assumptions placed by Pham were

- The frozen material has a single sharp freezing point at which all the latent heat is released.
- Below freezing point the material has a constant value of heat conduction.
- The sensible heat is concentrated in a single location point between the freezing interface and the unfrozen material.

According to Planck's equation of the freezing time and the sharp latent heat released point

$$t = \frac{1}{hA} \int [1 + f(Bi)] \frac{dQ}{T - T_a}$$
 Eq (2-19)

For the pre and sub-cooling stages the pure cooling heat transfer solutions still holds. Also since these periods are shorter than the freezing one, the sensible heat assumed to be lumped at a point between the surface and the cooling interface.

$$Q_2 = \lambda \Delta m$$
 Eq (2-21)

$$Q_3 = c_{ice}(T_f - T_c)V$$
 Eq (2-22)

The freezing time is thence the summing of the duration of these three stages,

$$t_{pre-cooling} = \frac{V}{hA} \int [1 + f_1(Bi_1)] \frac{dH}{T - T_a}$$
 Eq (2-23)

$$t_{phase-cahnge} = \frac{V}{hA} \int [1 + f_2(Bi_2)] \frac{dH}{T - T_a}$$
 Eq (2-24)

$$t_{sub-cooling} = \frac{V}{hA} \int [1 + f_3(Bi_3)] \frac{dH}{T - T_a}$$
 Eq (2-25)

Where	V	=	volume (m <sup>3</sup> )
	Α	=	surface area (m <sup>2</sup> )
	т	=	mass (kg)
	H	=	specific enthalpy (J/Kg)
	Т	=	surface temperature at a time interval $\Delta t$
	ΔT	=	the change in temperature with time
	$T_a$	=	the freezing gas temperature (K)
	Ti	=	initial temperature (K)
	$T_f$	=	freezing temperature (K0, it is found to be 1.5 K below the start of freezing temperature for material considered (meat or solid food)
	T <sub>c</sub>	=	centre temperature (K)
	$T_{fi}$	=	centre final temperature (K)
	Cl, Cice	=	the liquid and ice droplet specific heat capacity (J/kg k)
	Bi	=	Biot number, the internal resistance to heat transfer $=\frac{hL}{k}$
	L	=	surface length (m)

One other freezing model is of interest in this research is that of droplet, the most recent and more appealing model is that established by Hindmarsh et al (2003). He developed an experimentally approved numerical model for freezing a single droplet attached by a thermocouple in suspended in a cold air stream (Hindmarsh *et al.* 2003). In a typical scenario of spray freezing model, he considered that the governing equations and the physical properties of the drop are discontinuous for all the freezing stages. The model entails four stages of cooling (stages 1 and 4), freezing (stage 3) and supercooling and nucleation (stage 2). He reported three heat flux mechanisms playing role in the freezing process, first convective flux

$$q_h = h(T_{d,s} - T_a)$$
 Eq (2-26)

The second is evaporative cooling heat flux

$$q_m = \lambda h_m (\rho_{vd,s} - \rho_{va})$$
 Eq (2-27)

Finally a radiative heat flux,

The heat balance can calculate assuming the uniform temperature of the droplet for the cooling stages the transition

$$c\rho V_d \frac{dT_d}{dt} = q_h + q_m + q_r$$
 Eq (2-29)

The droplet in the freezing phase will have a conductive heat transfer, assuming the that the volume is constant and in one dimensional model the temperature transient starting from the surface (r = R) is

At the centre of the drop (r = 0) this temperature is

$$-k\frac{\partial T}{\partial r}\Big|_{r=0} = q_{th} \qquad \qquad \text{Eq (2-31)}$$

The solid volume fraction produced is determined from

$$V_f = V_d \frac{c_l \rho_l}{\rho_s} \frac{(T_f - T_n)}{\lambda_f}$$
 Eq (2-32)

Where

Thence, the freezing volume change within the drop (stage 3) at constant freezing temperature  $T_f$  determined from the following heat balance equation

$$\begin{array}{rcl} \lambda_f \rho_s \frac{dV_f}{dt} = q_h + q_m + q_r + q_h & \text{Eq (2-33)} \\ \\ \text{Where} & c & = \text{ specific heat capacity (J kg^{-1} K^{-1}) \\ h_m & = \text{ mass transfer coefficient (m s^{-1})} \\ q & = \text{ heat flux (Jm^{-2})} \\ r & = \text{ radial coordinate (m)} \\ R & = \text{ droplet radius (m)} \\ T_n & = \text{ nucleation temperature (°C)} \\ V_d & = \text{ volume of droplet (m^3)} \\ \mathcal{V}_f & = \text{ volume of droplet frozen (m^3)} \\ \mathcal{E} & = \text{ emissivity} \\ \sigma & = \text{ Stefan-Boltzmann constant} \\ \\ \\ \text{Subscripts} \\ \begin{array}{c} a & \text{ ambient air} \\ d,s & droplet surface \\ f & f & usion \\ h & \text{ heat transfer} \\ l & liquid phase \\ m & \text{ mass transfer} \\ r & \text{ thermal radiation} \\ \end{array} \right$$

solid phase 5

thermocouple th

#### 2.4.5 Freeze-drying modelling

A simple model for primary freeze-drying can be derived from a straightforward heat and mass transfer relations. Considering a case of drying a slab in a conventional freeze-dryer as in figure 14, the movement of water vapour through the porous layer is generalised by (Brennan 1990)

$$\frac{dw}{dt} = \frac{Ab(p_i - p_D)}{l}$$
 Eq (2-34)

Where	dw/dt	= water vapour mass flow rate through the dry layer.
	Α	= surface area parallel to the vapour sublimation flow $(m^2)$
	b	= the dry layer permeability (kg m/N s)
	$p_i$	= ice vapour pressure at a specific temperature (Pa)
	$p_D$	= water vapour partial pressure at the surface of the dry layer (Pa)
	l	= thickness of the dried layer (m).

Simultaneous heat transfer accompanies this mass transfer. In conventional freeze-drying process a substantial heat of sublimation is provided to the dried substance in a constituent with product quality, for increasing the rate of mass transfer. So the general equation for the heat transfer is

$$\frac{dQ}{dt} = \frac{k_D A(\theta_D - \theta_i)}{l}$$
Eq (2-35)

Where

 $k_D$ 

 $\theta_D$ 

 $\theta_{i}$ 

= the rate of heat transfer (J/s). dQ/dt = the dry layer thermal conductivity (W/m K). = the dry layer temperature (K). = the surface temperature of ice (K).



The energy balance of both equations is represented in

$$\frac{dQ}{dt} = \lambda_s(\frac{dw}{dt})$$
 Eq (2-36)

Where

 $\lambda_s$ 

= the latent heat of sublimation at operating temperature

$$\frac{k_D A(\theta_D - \theta_i)}{l} = \lambda_s \left(\frac{Ab(p_i - p_D)}{l}\right)$$
 Eq (2-37)

From Eq. (2-37) the thickness factor is cancel out, it is independent of the extent of drying. If the temperature of the dried surface temperature and the chamber pressure are fixed then the ice temperature is also fixed,  $\theta_i$ , and pi are thermodynamically related (Brennan 1990). The rate of mass transfer can be written as follow

$$\frac{dw}{dt} = A\rho_m (W_o - W_e) \frac{dl}{dt}$$
 Eq (2-38)

Where

We = moisture fraction in the dry layer at dry weight basis (kg). Wo = initial moisture content at the dry weight basis (kg). = the dried solid density  $(kg/m^3)$ .

From Eqs. (2-37) and (2-38),

 $\rho_m$ 

$$\frac{dw}{dt} = \frac{Ak_D(\theta_D - \theta_i)}{\lambda_s l} = \frac{Ab(p_i - p_D)}{l} = A\rho_m (W_o - W_e) \frac{dl}{dt}$$
 Eq (2-39)

The drying time is determined by integrating Eq. (2-39) for the following limits  $t_o = 0$ ,  $t = t_T$ ,  $l_{\rm o} = 0, \, l = l_T$ 

$$t = \frac{\rho_m (W_o - W_e) l_T^2}{2b(p_i - p_D)} = \frac{\lambda_s \rho_m (W_o - W_e) l_T^2}{2kD(\theta_D - \theta_i)}$$
Eq (2-40)

Where W, = the final moisture content (kg)

Form Eq (2-40) it is clearly seen that the drying time is proportional to the second power of the dried material thickness, therefore doubling in the slab thickness will prolong the drying time in Freeze-drying. While the dried solid permeability and thermal conductivity is dependent of the pressure and the nature of the gas in the pores (Brennan 1990).

#### 2.4.6 Advantages and Disadvantages of Freeze-Drying

Substances that are not damaged by freezing can be successfully lyophilized. Many microorganisms and proteins survive lyophilization well, and it is a favoured method of drying vaccines, pharmaceuticals, blood fractions, and diagnostics (Smith Donald 1963). Some specialist food products are also lyophilized. Freeze-dried materials dehydrate easily and quickly because of the porous structure left after the ice have sublimed. However not all foods can be freeze dried (such as lettuce and watermelon) because they have too high water content and freeze-dry poorly (Jennings 1999). Though lyophilization is not solely a preservation method, as used for biological materials, it is also a structural improvement process as it is used to produce high porosity ceramic super conductors (McGrath *et al.* 1992; Matsuda *et al.* 1993; Badica *et al.* 1996; Hampden-Smith *et al.* 1999).

Freeze drying yields the following benefits compared to evaporative drying methods

- Low temperature preservation, this feature reduces the effect of thermal damaging, as in many cases sub-freezing processing is required to avoid the chemical changes in thermo labile components.
- Low loss of volatiles, low temperature stabilisation also reduces the loss of volatiles to minimum. At low temperature, the vapour pressure of some substances is lower than that of water, hence the volatilise remains trapped with the solid matrix during the removal of water vapour at controlled conditions. (Flosdorf 1949).
- 3. No foaming, the low temperature stability of the structure also reduce the risk of foaming and bubble formation of the dried material unless the drying temperature is higher than the eutectic separation of temperature of the constituent, i.e. reducing the changes in the surface action of certain substances, for example blood plasma freeze-drying.
- 4. *Porous structure,* the freezing solidification of the dried material will form a framework of ice crystals in the solid concentrated solute matrix. Upon removal of the ice a porous structure is left, which exhibits excellent rehydration properties.
- 5. Reduction in solute diffusion, the stabilisation of the dried material matrix restricts its movements of the constituent during the drying process, this in term their diffusion toward the surface as the ice front recedes during sublimation inward to the centre. Hence casehardening is prevented by *freeze-drying*, as well as the tendency of coagulation (Flosdorf 1949).
- Hygienic, Although freeze-drying is a time consuming and slow process, the risk of microbial growth and contamination during processing is reduced, since the process is performed at low temperature (Goldblith et al. 1975; Mellor 1978).

7. Oxidation, The low pressure and temperature processing in this evaporation process reduces the possibility of oxidation occurrence (Jennings 1999).

The disadvantages of Freeze-drying are:

- 1. High capital cost of equipment (about three times more than other methods)
- 2. High energy costs (2-3 times more than other methods)
- 3. Long process time (up to 24 hour can be days drying cycle)

#### 2.4.7 Gas drying and dehumidification

The recent advances in gas drying processing aims to reduce the problematic incidence in a non-interrupted operation, as well as the potential cost reduction by energy and environmental saving of purification or recycling (Perry *et al.* 1997);(Richardson *et al.* 2002). Gas drying methods applied in industries are the following

- Dry desiccant plants
- Glycol adsorption or injection plants
- Low-Temperatures or refrigerant expansion plants.

In a freeze-drying operation shortening the path between the condenser and the drying chamber is crucial for a successful drying operation, as this helps reduce the risk of desorbing the removed vapour back into the dried material by transferring it to a higher adsorptive capacity surface. In a typical designs a freeze-driers usually condenser is used (Mellor 1978; Jennings 1999; Oetjen 1999). Research on fluidised bed freeze-drying by Wolff et al, (1991) had used whey as an adsorbent inside the bed to remove the sublimed moisture by adsorption from biological materials, intending to reduce the vapour travelling path.

Generally the selection of a suitable method of gas drying is based on two practical factors; first is the cost of the plant installation and operation, and the second is the specific application. The simplest and practical gas drying method used is the dry desiccant techniques, however the main draw back obstacle is the limited adsorption capacity of the

desiccant solids. Adsorption gas desiccation or drying process is achieved by passing a humid gas stream on unsaturated adsorbent. Adsorbents have a high chemical affinity to bound water within its structure, though it is easy separated by regeneration of adsorbent using a gentle heat drying. The adsorbents are characteristically inert with a high surface area through large value of porosity.

Adsorption process is a physical-chemical separation technique that is an effective removing and/or recovering technique of a trace component from a flowing feed or process effluent stream. The adsorbate molecules in a carrier inert stream physically diffuse through the surface of adsorbent and bind specific receipting binary atoms composing the adsorbent surfaces by weak reversible forces, Van der Waals and/or Electrostatic force <sup>(170, 172, 174)</sup>. The most common adsorbent used in industrial and laboratory scale adsorption drying processes are Activated Alumina, Molecular sieves, and silica gels, which are characterized by high porosity and adsorption surface area as well as affinity to water binding due to the hydrophilic polarity nature. However, their adsorptive capacity varies with manufacturing specification, size, type, and polarity (Carter 1968 1971).

The adsorption dynamic is a result of the equilibrium state achievement between adsorbent and the carrier flow medium, at which the rate of adsorption is equal to rate of dsorption at the adsorbent surface. Adsorption rate determination is a function of the pressure and temperature in a relationship that links the adsorbed phase (gas) and the unit mass or surface area of the adsorbent in a formula. Three parameters influencing this equilibrium status that must be considered by a designing engineer to obtain relative accuracy since the adsorption calculations is base on number of assumptions as seen later; adsorbate concentration in the flowing phase best represented in partial pressure, then adsorbate concentration in the adsorbent surface, and finally the process temperature. Often to present the Equilibrium State of adsorption, one of these three parameters is kept constant, i.e. the volume of the adsorbed phase plot against concentration at constant temperature and variable pressure is called isotherm, while this plot at constant pressure and variable temperature is known as a isobar, from these plots a variation of the equilibrium with temperature and temperature of a fixed volume of the adsorbate could be observed or represented. The equilibrium capacity of the adsorbent is also dependent on their structural characteristics, which in turn influences the selectivity passage of the adsorbate molecules into the pores according to their size hence the adsorption surface area.

In low-pressure operations, the vacuum influence on the gaseous environment of the drying system described based on the kinetic theory of gases. The vacuum affects the motion of the gas molecules and or atoms movement, which in turn influences the gas-gas molecule collisions or gas-wall or surface molecule collision (Delchar 1993). For the Knudsen or viscous gas flows of adsorb able component onto a barrier of adsorbent the collided adsorbate molecule with the surface of the adsorbents forms an adsorbed film on the surface that is negligible in volume in comparison to the pore volume. The mechanism of the Knudsen flow assumes that adsorption continue on the surface of the adsorbent until it goes into a diffusion reflection (Carman 1956).

Rowe & Powel in 1981 studied the freeze-drying process by adsorption. They had classified the adsorbent as a dual role agent of heat and mass transfer, based on the fact that the external heat transfer is much better as the sublimation magnitude is of the same order of the adsorption which leads to lower energy requirement of freeze-drying (Lombrana *et al.* 1997).

Then for freeze-drying operations adsorption is possible if the adsorbent temperature of the system is low enough to maintain site attachment and the adsorbate vapour partial pressure in the adsorbent is lower than that in the system (Zhukova *et al.* 1962).

#### 2.4.7.1 Humidity, temperature and pressure relations

Normal air may contain a certain amount of water vapour, variable between 0 to maximum saturation level. The gas normally contains less vapour than its capacity as a result of water evaporation from wet surfaces, including ice that this stream is in contact with. The amount of this water varies with temperature and water availability, total pressure and whether the air is near to a water or ice surface. The reason of this water uptake and phase change of liquid to gas is a result from the air tendency to be in an equilibrium state with contacted surfaces. In the real system a gas stream contain a certain a mount of vapour less than it does maximum

saturation capacity. This report illustrates a collection of some, formulae and texts that reflect on connections of temperature, humidity and dew point temperature.

#### 2.4.8 Freeze-drying process measurements - rate of mass transfer

The quality measure of freeze-drying process expected is largely and adequately dependent on the residual moisture content, during and after processing (Baradat *et al.* 1993; Genin *et al.* 1996). The sublimation end point determination is an essential indication of the end of processing time, especially in the case of freeze-drying since it is a high cost and time consuming process (Roy *et al.* 1989). The Residual Moisture Content (RMC) determination methods generally prescribed in term of their mode of detection and contact with the measured sample, i.e. direct/indirect, contact/none-contact, and online/or offline analysis methods. In direct methods attempt to evaluate the RMC by tracing the physical properties and changes of water in the system, such as water vapour pressure measurement in the surroundings, temperature changes of the dried material, and electrical capacitance changes of the desiccant (Konstantinove 1980; Roy *et al.* 1989; Baradat *et al.* 1993; Genin *et al.* 1996).

The complexity of freeze-drying system design and its batch like operation presents practical difficulties in carrying an online direct moisture analysis of the process and material. These difficulties result from the unusual operational conditions of the freeze-drying process, such as drying under vacuum and low operation temperature. The alternative is to perform this analysis off line. However, such procedure may implicate further difficulties. For example, sample collection from the vacuum closed system with out interfering with the system operational conditions, and handling the collected sample outside the drying rig bearing in mind to minimise or eliminate external effects on the sampled material, such as external condensation.

#### 2.4.8.1 Direct-Off Line Methods of RMC Measurement

Sample Extraction followed by gravimetric analysis, using standard mass transfer laws. A specially constructed sampling device will be attached to the drying chamber (see figure 19) This device penetrates the system and collects a desired sample with minimal interference with the system operation or condition. This technique has the advantage of flexibility in performing different types of off line analysis. The moisture content analysis can be

performed using vacuum drying oven. In this method a sample of a known weight dried material are collected at time intervals and dried in a vacuum oven for 24 hours at 100 °C. The dried sample is re-weighed and the difference in weight represents the mass of moisture removed from the sample.

#### 2.4.8.2 Indirect-Online Methods of RMC Measurement

# 2.4.8.2.1 Partial vapour-pressure in a vacuum freeze-drier

At the beginning of the freeze-drying process the vapour partial pressure surrounding the dried material is zero. Upon freeze-drying, the dried material loses vapour that transferred into the surrounding gas phase where the vapour partial pressure of the surrounds rises toward the saturation condition at that temperature. The measurement of vapour partial pressure of the out going gas at the exit point and comparing it to that of the inlet point can therefore indicate the amount of moisture removed from the processed material (Baradat *et al.* 1993).

The recommended apparatus for the vapour pressure measurement is the Pirani gauge used to determine the end of sublimation point, primary drying. The measurement mechanism depends on variation in the gas composition sensed by a thermal conductivity gauge. At the start of the sublimation vapour partial pressure will increase which increases the displayed readings of the pressure gauge. At the sublimation end-point the partial pressure of water vapour stabilises in the system, vapour partial pressure, due to the completion of ice removal and so the Pirani gauge readings stabilises. This method of moisture measurement is relatively cheap, non-invasive, easy to perform and interestingly independent of the process design and shape. But a question mark remains over the level of sensitivity and the ability of using this measuring apparatus for detecting the secondary drying stage (Baradat *et al.* 1993).

#### 2.4.8.2.2 Electronic moisture sensors or hygrometers

This sensor measures the partial pressure of water vapour in a gas stream, it is a precise and most accurate in detecting the end-point of sublimation (Roy *et al.* 1989; Baradat *et al.* 1993). The measurement mechanism of the sensor depends on the change in the electrical capacitance of a thin film of aluminium oxides ( $Al_2O_3$ ) when absorbing water from the surrounding phase. The instrument then translates these changes into a voltage output that is <u>calibrated to read the partial pressure of water or its frost point. Considering this measured</u> *An Investigation of Spray-freezing & Spray-Freeze-Drying* 59

value of vapour of the removed moisture in the drying medium with the desired level in the final product, we can determine the end of drying process, according to the findings of Genin et al. 1996. This method determines the Sublimation End Point as a function of time SEP(t), the dehydration rates of these time intervals are relatively equal until they reach the sublimation end point, where the mass flow rate is zero. This is explained by the following formula

$$SEP(t) = \left(\frac{P's - P'c}{P_T}\right) - \log\left(\frac{P_T - P'c}{PT - P's}\right)$$
Eq (2-41)

Where

SEP (t) = the sublimation end point at t time

D <sub>T</sub>	= the total pressure in the system (Pa)
ס' <i>ג</i>	= the vapour partial pressure of the sensor (Pa)

P'c = the vapour partial pressure at the condenser (Pa).



Figure 2- 19: Conversion chart of dew point temperature vs. pressure (Wiederhold Pieter 1997).

Pikal et al (1989) stated that monitoring the partial pressure gauges under constant total pressure serves as an end of sublimation detection system, which agrees with the above formula. The water vapour information is also a relevant parameter in the freeze-drying processes as it is consists the major driving force of the mass transfer mechanism (Roy *et al.* 1989; Genin *et al.* 1996).

#### 2.4.8.3 Freeze-drying conditions effect on humidity and its measurement

Generally the freeze-drying process operates at temperature below 0 °C and pressure as low as 613 Pa. At low temperature environment the humidity or the water vapour concentration tend to be very low or measured by ppm<sub>v</sub>, as well as the dew point is lower by 10-15 °C of the operating temperature (Carr-Brion 1986). Though adding the factor of low pressure to this conditions tend to further depress the dew/frost point, while increasing the gas vapour up take capacity (saturation) with lowering the pressure (Wiederhold Pieter 1997), see figure (2-17).

In the last decade few research scientists took the liberty of the technical advances in the field of moisture trace detection in a gaseous environment of a freeze-drier. Their intention focused on mainly on the advantage of using humidity sensor as an online measuring device of freezedrying process. The final conclusion has drawn to the online vapour pressure detection using humidity sensor as a best mean of process control and measurement.

#### 2.5 Atmospheric Freeze-Drying

Sublimation of ice as pointed earlier occurs at temperatures and pressures below the Triple Point. But it is also possible at high overall pressure as long as the temperature is below the triple point temperature of water, so long as the water-vapour partial pressure is below the saturation value. Atmospheric freeze-drying occurs naturally and on a large scale when ice sublimes in open places such as Antarctica. In the domestic freezer, ice sublimation also occurs and causes drying of unwrapped foods over a long period of time. Thus atmospheric freeze-drying is nothing new, although the slow rate of drying encountered in this system poses difficulties for any commercial process (Noyes 1968; Mellor 1978; Jennings 1999; Oetjen 1999).

At a stabilised temperature (with no ice crystal melting or growth), Meryman (1959) had presented a water vapour removal analogy as exist in freeze-drying operation;

The rate of which the water-vapour molecules leave the frozen matrix is purely depends on the ice crystal temperature. Sublimation is therefore would be sufficient if the rate vapour removal adequately preventing the leaving molecules from returning to the ice surface. Although, the sublimation is resisted by first the diffusion capacity of the water-vapour molecules through the dried layer, which is dependent on

- Rate of vapour production or the ice temperature.
- Vapour diffusion resistance through the dry shell or layer of the specimen.
- The partial vapour pressure at the surface of the specimen.
- The second obstacle to the rate of sublimation is the vapour diffusion resistance in the vapour sink medium (vapour trap).

Vacuum application in conventional freeze-drying aims to facilitate the transfer of the leaving water-vapour molecules from the dried specimen into the vapour sink or trap by reducing surrounding resistance and arranging a long free mean path to vapour trap, while minimising molecule collisions.

From this analogy it is clear that vacuum application is not a necessity, if one can apply other means to reduce the resistance effect to the rate of water vapour removal from the frozen specimen. He also confirmed that the vapour pressure passage through the dried material in the freeze-drying process depends on the partial vapour pressure gradient rather than overall pressure of the system. Upon this he successfully managed to atmospherically freeze-dry a 2 (mm<sup>3</sup>) sample of mouse kidney tissue at -30 °C using a continuously circulating desiccated air (Meryman 1959).

Malecki et al. (1970) pursued this lead to freeze-dry an aqueous solution sample by fluidisation under atmospheric conditions, and achieved a desirable result. Though Malecki added one fact to this analogy that is the freeze-drying controlling rate is the water-vapour diffusion resistance through both (dried and drying) mediums. This resistance is proportional to the diffusion path permeability of the dried material. Hence reducing the specimen size would accelerate the rate of atmospheric sublimation by shortening the vapour molecule diffusion path. He designed a fluidised atmospheric freeze dryer, and investigated the performance and drying possibility of this process by drying apple juice, liquid egg, and orange juice (Malecki *et al.* 1970).

Other researches such as Woodward (1963) looked into the economical sides of atmospheric freeze-drying and he found that operational cost is equivalent to that of conventional freeze drying method (Woodward 1963; Noyes 1968). Heldman (1974) established a mathematical model of atmospheric freeze-drying process that evaluated the mass and heat transfer parameter involved as well as the operational conditions that affect the process. Boeh-Ocansy et al. (1983) examined the sublimation rate of a number of same products with specific dimensions in fluidised bed using an adsorbent granules in the aim or reducing the vapour molecule travel path to the vapour trap, and found that atmospheric freeze drying time is far shorter than the conventional freeze drying for a product with a large surface area. In similar researches of reducing the vapour molecule paths there are many researchers presented a viable findings in different fields of material drying such as Tutova et al (1988), Wolff and Gibert (1990), and Carmen et al (1997). Though this approach has its complication of sorbent separation at the end of the drying operations. Leuenberger et al. (1990) successfully developed an operational system investigating the drying quality of atmospheric freeze-drying

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using the advantages of all above findings to achieve a flow able fine porous dry dried material at a reasonable drying time. Though, his work is a design and experimentally oriented.

#### 2.5.1 Modelling Atmospheric Freeze-Drying

The mathematical module of atmospheric freeze-drying set by Heldman in (1974) is described by the two equations, the first is represents the heat transfer and the second represents the mass transfer of atmospheric sublimation (Heldman 1974).

 $\rho_B \left( D_{pd} + Mc_{p_w} \right) \frac{\partial T}{\partial \theta} = \frac{\partial}{\partial \theta} \left( \frac{k}{D} \frac{\partial T}{\partial \phi} \right) + \frac{D_e}{D} c_{p_w} \frac{\partial p_v}{\partial \theta} \frac{\partial T}{\partial \phi} + \rho_B \Delta H_v \frac{\partial M}{\partial \theta}$ Eq (2-42)

$$\left[\frac{eM_{w}}{RT} + \frac{\rho_{B}}{p_{sat}}\left(\frac{dM}{dr}\right)\right]\frac{\partial p_{v}}{\partial \theta} = \frac{\partial}{\partial \phi}\left(\frac{D_{e}}{D}\frac{\partial p_{v}}{\partial \phi}\right)$$
 Eq (2-43)

Where	$ ho_B$	= bulk Density of a porous zone $(kgm^{-3})$
	θ	= $Dt/s^2$ , dimensionless time, as t is time (s)
	$\phi$	= x/s, dimensionless distance
	C <sub>pw</sub>	= specific heat of water at constant pressure $(Jkg^{-1} \circ K^{-1})$
	D	= mutual free-gas diffusivity, air and water vapour $(m^2s^{-1})$
	Dpd	= diffusivity of the dry product $(m^2s^{-1})$
	De	= effective water vapour transfer diffusion coefficient = $\frac{C_2 \overline{D}M_w}{PRT}$
	$\overline{D}$	= DP, (m <sup>2</sup> . Pa.s <sup>-1</sup> )
	$C_2$	= constant dimension less
	е	= porosity of the porous zone, dimensionless
	k	= effective thermal conductivity, porous zone, $(Wm^{-10}K^{-1})$
	М	= moisture content dry bases (kg)
	$M_w$	= molecular weight, water (kg.kg <sup>-1</sup> mole <sup>-1</sup> )
	Р	= total pressure (Pa)
	<i>p</i> sat	= saturated vapour pressure (Pa)
	$p_{v}$	= partial vapour pressure of water (Pa)
	R	= universal gas constant ( $m^3$ .Pa.mole <sup>-1</sup> .°K <sup>-1</sup> )
	Т	= temperature in the porous zone (°C)

x = distance (m)  $\Delta H$  = heat of vaporisation, sublimation (Jkg<sup>-1</sup>)

Appropriate boundary conditions are required to solve equations (1) and (2), which they should be solved simultaneously to yield temperature and vapour pressure at all points as a function of a dimensionless time. Heldman conclusion was "the moisture removal in atmospheric sublimation is a non-linear estimation relation, while the heat transfer through the sample is by conduction through a solid matrix". The reduction in the sample sizes is the most effective way of increasing the sublimation rate, due to mass transfer coefficient increase (Heldman 1974).

A simpler model set by Boeh-Ocansy et al. (1983) whom investigated the kinetics of ice sublimation at atmospheric pressure and modelled as the rate of sublimation is a function of square reciprocal total drying time, it is illustrated by the following expression (Boeh-Ocansey 1983; Boeh-Ocansey *et al.* 1986)

$$\frac{M}{M_o} = \left(1 - \frac{t}{t_T}\right)^2$$
 Eq (2-44)

Where  $M_o$  = initial moisture content, dry basis (kg).  $t_T$  = total time (s).

Yet it is a clear that, there is no a unified design and drying modelling trend for approaching the atmospheric freeze-drying process. In this intention establishing a practical heat and mass transfer model for the atmospheric freeze-drying process becomes a task of this research. Then validating the established process model experimentally, using accurate heat transfer evaluation of both freeing and sublimation stages by accurate characterisation of the dried matter in term of physical properties. Thereby the next reported material is of the proposed drying process design and consideration.

## 2.6 Conclusion

The proposed spray freeze-drying process of this research is a controlled instantaneous spraying and freezing operations followed by duration of sublimation in controlled pressure environment. This technique may ensure high-quality particles production, and eliminating the solute migration effect by stabilising the solution in a solid matrix with interstitial ice crystals within a particle, that leaves voids after drying and good pore size distribution. The case of solute solvent separation is also tuned down in the case of spray freezing by small crystal formation result of rapid freezing process. The particulate size control in the spray freezing process gives a reasonable degree of size homogenisation, pending on the spray nozzle type and operation pressure.

The material presented in this chapter laid the vision of the proposed spray freeze-drying process design and the operational criteria required for the process control. Form the spray drying section we drawn to a conclusion of adopting small narrow spraying chamber employing nozzle atomiser for the spray generation. The fluidisation section helped in planning the operational thought of the residence time and trying control. The freeze drying section conclusions are

- Spray freezing in a gaseous environment will help produce larger ice crystals and lower the supercooling duration of the drop, hence reducing the freezing time by lowering the resistance to vapour diffusion and producing particulate with good porosity.
- Freezing completion of the drop is a critical step in producing a quality powder of ice eliminating the risk of making snow like particles due to agglomeration. Therefore the adoption of a reasonably accurate freezing model (spray freezing) helps predicting the operation control in the process.
- The success of the freeze-drying operation is dependent on the temperature and pressure control of the operation unit to avoid material collapse.
- The gas dehumidification can be a tool to desiccate the freeze-drying gas employed in the fluidisation process.

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• The process length can be predicted from the humidity or vapour pressure of the drying gas between the inlet and outlet points of operations vessel, however adopting a more representative mass transfer rate determining method (sample weighing) would be a bonus to this research.

Finally the process success evaluation will be based on the end products quality comparison with that of spray drying, spray freezing and conventionally freeze-dried samples. The drawn conclusion shall be formulated in the next chapter, of experimental rigs design. ...!

# Chapter 3

Process design and construction of experimental rigs

#### 3.1 Introduction

#### 3.1.1 Outline of proposed process

The literature relating to spray-freeze-drying has been described in Chapter 2. The advantage of spray-freeze-drying techniques over conventional freeze drying processes is the high surface area to volume ratio and small diffusion distances generated by atomisation, which is able to dramatically reduce freeze drying times. However use of the method is still quite rare. The aim of this research is to examine current methods and investigate possible process modifications with the aim of economically and efficiently producing high quality freeze dried powders for a range of industry sectors.

The most recent research in this field is by Leuenberger et al (1991) who has adopted the atmospheric spray-freeze-drying process, whereby very dry, freezing air is circulated through a fluidised bed containing the frozen particulates. Sublimation can occur so long as the partial pressure of water vapour is below the saturated vapour pressure of ice at the temperature of the particulates. However, most freeze-drying must be performed at temperatures below – 30°C in order to avoid collapse of the particulate structure. At these temperatures the saturated vapour pressure is extremely low (38.96 Pa at -30°C). Even if freeze drying had no kinetic constraints and the exit air of the fluidised bed were completely saturated it would require (by use of the Ideal Gas Law) 4188.82 kg of bone dry air to pass through the bed in order to sublime 1 kg of ice. Although this can be partly offset by re circulating (and drying) the air, this is a huge quantity of air to be supplied to the process. The refrigeration and drying requirements on such a mass of gas to meet the required specification are considerable and would severely harm the economics of the process. A further consideration is that to pass this mass of gas through the bed in a reasonable time (say a few hours) requires a very large gas volume flow rate and hence velocity. This leads to particles being rapidly swept out of the fluid bed where they must be caught by an air-filter (Mumenthaler et al. 1991). Although this is a feasible means of drying the particles, it does render the fluid bed (with its high heat and mass transfer ability) redundant.

One means of circumventing this problem, which does not appear to have been considered by Leuenberger is to apply a partial vacuum to the process. The air is, after all, merely an inert filler gas and plays no part in determining the driving force for mass transfer. As an example, if the process is operated at -30°C and at 0.1 bara then the mass of gas required would be 418.88 kg (i.e. one tenth of the amount at 1 bara). A vacuum capability would increase the capital cost and operational difficulty of the plant, but also significantly reduce the mass of dry air required. An initially rather startling result is that the volume of gas to sublime 1 kg of ice (assuming saturation) is independent of system pressure (in the above examples 2891.93 m<sup>3</sup> of air would be required in both cases). This is because even though there is ten times less mass of gas required at 0.1 bara, the reduction in pressure by a factor of ten means that the gas is also ten times less dense. By the same token to extract this 1 kg of ice, the gas velocity passing through the bed would also be the same irrespective of total system pressure. However, the lower density at lower pressures would reduce the drag force on the particles, and if a low enough pressure were used then particles would not be swept from the bed.

Thus lower pressures are desirable as they decrease the mass of gas required and reduce particles being swept from the bed. One could thus postulate that the higher the vacuum the better, and this would suggest going down to the pressures used in conventional freeze drying (with effectively no air in the system). This is similar to spray freezing followed by freezedrying in a conventional freeze dryer. The difference is that freeze dryers have a source of radiant heating to supply the latent heat of sublimation. However, this form of heating is not well suited to the uniform heating of powders as it does not make use of the high surface area to volume ratios, as it will only directly heat exposed surfaces. In our process the aim is to supply the latent heat from the fluidising air, but this will not be available if there is no air. Thus one can postulate that there might be an optimum pressure of operation, which is low enough such that a small mass of air is used, and high enough that the particle temperatures can be maintained. The existence and location of an optimum pressure between the two extremes of high vacuum and atmospheric pressure is one of the major questions we wish to examine.

To this end a spray-freeze-drying rig was constructed, based upon the Leuenberger process, but including the capability of applying a vacuum. The rig is fully instrumented to allow online measurement of gas humidity, temperature, pressure and sample mass to gain a quantitative understanding of the different mechanisms at play.

# 3.1.2 Investigation of spray-freezing

The spray freezing process is a critical part of the spray-freeze-drying process on two main counts (i) the atomisation governs the overall particle size distribution, and (ii) the rate of cooling of a droplet affects how ice crystallises in the droplet. This affects the number, size distribution, shape and locations of ice crystals within the frozen droplet (i.e. the internal structure of the particle). During the freeze-drying stage these crystals sublime to leave voids, resulting in a porous structure, which is determined from the frozen ice structure. The particle size and pore structure are obviously important product characteristics, but they also influence the kinetics of the subsequent freeze-drying process. Particle size influences factors such as surface to volume ratio, diffusion distances and terminal slip velocities, whereas pore morphology influences the rate of primary sublimation - a small number of large interconnected pores are likely to sublime faster than a large number of small isolated pores.

The importance of the spray freezing process to the process as a whole led to a separate investigation to be made into the spray freezing process. This was undertaken using the Phase Doppler Anemometry technique, which is well adapted to the characterisation of spray systems. The method allows the diameter and velocity of hundreds of thousands of droplets passing through a small control volume to be measured in a single second.

These measurements enable (i) the atomisation conditions to be adjusted to optimise homogeneity of the spray population (ii) the size distribution of the sprays to be measured (iii) the velocities of different size drop classes to be assessed.

The simultaneous measurement of size and velocity for individual drops is an extremely powerful probe to investigate spray-freezing conditions, and can be used to test models of spray freezing. It is probable that CFD type models may be necessary to accurately model spray freezing, but some simple spreadsheet models have been attempted. Although lacking in sophistication it is often possible for simple models to shed light on experimental observations, in particular in how a real system differs from a simple "ideal" system.

A final line of investigation was to examine the possible use of the PDA technique as a probe of the solidification process itself, due to the different optical properties of solid particles and liquid drops.

# 3.1.3 Comparison of spray freezing in cold air and in liquid nitrogen

Current methods of spray freezing generally involve spraying into either (i) a cold gas (i.e. the method used above) or (ii) a cold liquid (e.g. liquid nitrogen). A further series of experiments were thus also planned to compare the results of spray-freeze drying after spray freezing in cold gas or in liquid nitrogen. It is envisaged that liquid nitrogen will cool the particles much more rapidly, and create a finer porous microstructure. This would thus affect particle morphology and also be likely to affect the rate of freeze-drying.

# 3.1.4 Overview of experimental used in this research

It was thus required to construct three experimental rigs for the project

- The design and construction of a spray freezing chamber equipped with windows to permit Phase Doppler Anemometry studies of drop sprays under ambient and sub-ambient conditions which are described in Chapter 5. The details of this rig are given in Section 3.2.
- ii. The design and construction of a full spray-freeze-drying system for the experiments described in Chapter 6. This was able to use the spray-freezing chamber from the PDA experiments, as part of the design. The extra items required for this rig and their method of assembly are described in Section 3.3.
- iii. The construction of a cryo-spray-freeze-drying system (i.e. freeze drying after spraying into liquid nitrogen) is described in section 3.4. This used a separate spray-freezing rig from which material was then transferred into the freeze-drying fluidised bed detailed in Section 3.3.

The proposed process consists of the following operations, see figure (3-1)

- Spray freezing, by atomising a liquid feed into a very cold stream of nitrogen gas or liquid at atmospheric pressure, which induces droplet freezing.
- 2. Separation of the frozen droplets from the carrier gas stream by a cyclone.
- Collection of the frozen particulates in a fluidisation chamber where freeze-drying by flowing dry gas at sub ambient temperature and atmospheric or sub atmospheric pressure takes place.
- 4. A vacuum pump is used to regulate the pressure in the fluidised bed between full vacuum and atmospheric pressure.
- A desiccant is used to dry the gas and reducing the load on the vacuum pump and also dried gas to be re circulated back into the fluidised bed.
- The temperature into both the freezing chamber and fluidised bed is controlled by supplying from combining a mixture of liquid nitrogen with nitrogen cylinder gas in a variable ratio.





#### 3.1.5 Design criteria and features of concern

One disadvantage of the conventional freeze-drying process is the noticeable decline in the rates of heat and mass transfer after commencement of drying due to the low thermal conductivity of the dried material in a vacuum. The suggested solution is to operate in a cyclic pressure system, but with a time lag in the control system this could increase the risk of melting and collapse of the freeze-drying operation.

In the spray freeze-drying process proposed the partial vacuum or low pressure alone can be advantageous operation process development technique to increase the rate of heat and mass transfer by increasing the thermal conductivity of the gas and solid phases. In addition of lowering the density of the gas volume inside the system thence reducing the resistance of the vapour diffusion into the gas phase and lower the potential of the particle carry over loss from the fluidisation freeze-drying as reported by Leuenberger et al.

The anticipated problem in the ASFD process is particle agglomeration. Malecki et al, (1970) reported in his research on atmospheric spray freeze-drying of apple juice and egg albumin solutions that above certain temperature agglomeration takes place due to the increase in the particle stickiness, which interrupts the overall drying process. The stickiness results from the incomplete freezing of the concentrated liquor in the particles. To avoid stickiness one need to operate at temperatures below the eutectic melting point or the glass transition temperature (i.e. collapse temperature), which are characteristic of individual products and their solid content. Above this temperature particles form liquid bridges between themselves. The spray freeze-drying process operated in a temperature 5 °C below the material collapse temperature, and the latent heat of sublimation would be provided by the freezing-drying gas.

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## 3.2 Spray characterisation rig

Spray freezing is the first major operation of the spray freeze-drying process. The critical concern of this operation is solidifying the atomised feed before it contacts the chamber wall to minimise the adhesion of particles to the chamber wall. This may alleviates corrosion, contamination problems, processes failure, and loss of production. Therefore it is necessary for the spray chamber to be sufficiently sized. This is a similar problem to that encountered in spray drying where the droplet surface should be sufficiently dried before it is liable to contact with the chamber wall.

The design of the spraying chamber dimensions must take into consideration the droplets size, its trajectory path through the chamber and finally the rate of freezing. The principle design to be made was whether to adopt a rotary atomiser in combination with wide chamber or a nozzle type with a tall form chamber. A nozzle system was preferred as it was considered easier to heat (to avoid freezing of the liquid feed) as there are no moving parts. The associated tall form chamber was also advantageous as it takes up less floor space. Masters (1991) recommended that the dimensional specification of a chamber with spray nozzles should have a minimum 3:1 diameter to length ratio. The chamber size was based on the requirement to produce particles sizes up to  $500 \,\mu\text{m}$ .

It was decided to incorporate a degree of flexibility into the chamber design to allow (i) different configurations of spray freezing (counter or co current), and (ii) the exact vertical positioning of the spraying point at the top of the chamber to be variable, to aid the spray measurements as will be seen later in chapter 5.

The space and size of the chamber was decided based on experiments to find the spray trajectory and coverage cone of a siphon round pneumatic nozzle (XA Sr50). The nozzle operated to produce a mist of water in open air at pressurised air feed up to 3 bar and liquid siphoned through the nozzle. Visual observation were made of the distance the spray travelled before essentially stopping (velocity of only few centimetres per second). This distance extended to 1.5 m down ward from the nozzle orifice and the angle of spray cone was

relatively narrow (less than 45°). The chamber was planned to be conical tall shape with a slight excess of space to permit plenty of time for the drop freezing to take place before it can contact the chamber wall. Our initial calculation shows that in many cases the drop freezing occurs in less than 1 second.

The gas flow configuration in the chamber was design to be flexible between co-current and counter-current. Both modes of operation would be tested in order to determine which was the more successful.

The chamber was designed in three sections (i) top cone housing a the opening for the atomiser and the chamber gas in or outlet, (ii) cylindrical section of spray characterisation measurements, and (iii) the bottom cone in housing the particles outlet and gas inlet or outlet. A sketch of the chamber with dimensions is showing below.





The chamber 2.01 m height in total was made of 1 mm thick mild steel sheet. Therefore chamber inner wall was painted with a "mat-black" acrylic paint coat strengthened with heavy duty metal primer under coat. This was to protect the chamber from corrosion and to absorb light from any stray beams from the PDA laser measurements to minimise the health and safety risk.

Starting from the top cone section of the chamber showing in figure (3-3), it is 0.16 m high with two gas inlet/outlet openings position at 180  $^{\circ}$  from each other attached into a circular groove channel. The opening diameter is 0.14 m in diameter where as the bottom end is 0.8 m welded to flange attaching this part to cylindrical section.

The cylindrical section had special windows fitted (of 100 cm long and 10 cm wide) to permit the phase doppler anemometry (PDA) measurements, see figures (3-4) and (3-5). These windows were made of heat-treated glass to withstand thermal shock of the freezing operation. These glass windows were removable so that they could be easily cleaned and were each fastened into the main frame by two 100 cm long "L" shaped bars on each side that secured to special frame welded onto the chamber. Five windows were fitted on to the chamber four of them were required for the PDA measurements where as the fifth window is designed for the photographic imaging of the spray

- i) A window for the laser inlet  $(0^{\circ})$
- A window for the laser outlet (180°) to allow alignment of the laser beam during setting up.
- iii) A window to allow the collection of the refractive scatter. This occurs at a maximum (70°) to the incident beam and thus the window positioned accordingly.
- iv) A window to allow the collection of reflected scatter. This occurs at (110°) of the incident beam. This window was not used for this research but was built in this design for a future work.
- v) A window for the photographic imaging of the spray positioned at (270  $^{\circ}$ ).

The windows were sealed onto the chamber frame by a specially moulded silicon seal, providing a flat cushioning to the glass. A spongy type draft excluder strips were attached on the front edges of the glass, to minimise the air leak and providing protection to the edges from chipping.



Figure 3- 3: The arrangement of the top cone in the chamber illustrating the gas lines and the and positioning of the spray point.



Figure 3- 4: AutoCAD drawing of the window design and arrangement in the chamber cylindrical section.



Figure 3- 5: Cross section view of the cylindrical section.



Figure 3- 6: The lower cone and gas-particle separation box.

At the end of the spray freezing chamber a particle collection box was attached into the lower opening of the bottom cone (see figure3-5). The produced particles will be driven into the box and separated from the gas stream, which is vented to the exhausted ventilation extractor.

The chamber with exception of the glass windows was fully insulated with 25 mm thick "High Temperature Armaflex" sheeting.

## 3.2.1 Gas and freezing medium

Liquefied nitrogen  $(LN_2)$  cooling source was preferred to using air refrigeration system (cascade type) for the following reasons

- i) Low cost
- ii) Greater flexibility
- iii) Much higher cooling power
- iv) Very low humidity of nitrogen gas generated from  $LN_2$  which would assist in the freeze-drying part of the research. Refrigerated air on the other hand would have higher relative humidity.

Liquid nitrogen poses a suffocation risk if used in any thing other than small amounts. This problem can be overcome by adequate insulation, system pressure control, good ventilation, and environmental monitoring of oxygen levels.

The freezing system proposed mixes  $LN_2$  supplied from an external dewer with  $N_2$  gas from a cylinder in a vaporisation chamber. The incoming liquid refrigerant is vaporised in the gasifier vessel (see figure 3-7) by atomising the flow of  $LN_2$  and mixing it with nitrogen from pressurised compressed cylinder. The ratio of the flow liquid nitrogen and nitrogen gas was regulated by a manual needle valve to each stream to obtain the set temperature and flow of operation conditions required, in particular that at the spray release point. Nitrogen gas was also used to initially purge the process lines and vessels from any humid air or condensate at the beginning of each experiment. This would then be followed by introducing  $LN_2$  into the chamber to cool the apparatus to the target temperature in a reasonable time frame.

The flow mixer/vaporiser is a pipe of dimensions 100 mm id X 600 mm long pipe is blanked with two flanges at both ends. At one end one pipe feeds supply of  $LN_2$  and two others supply nitrogen gas. At the other end one line was used for a pressure release valve and the other is the outlet which into the distributor of spray freezing chamber. This gasifier design had a number of considerations to be met during operations as desired such temperature, pressure, flow and its quality. Not least important the safety characteristics, strength and operation simplicity of the gasifier is maintained. The freezing medium (liquid and or gas) forwarded from the mixing vessel into the spray freezing chamber in a different format depending of chamber operation configuration counter or current flow.

In the counter current configuration the flow is introduced into a manifold feeding four lines that are connected through the wall of the lower cone of the chamber at  $90^{\circ}$  intervals. These inlets (which can be separately regulated) lead the flow evenly to silicon cured circular pipe distributor, which is drilled with a number of rows of 3 mm diameter orifices in both upward and down ward directions, see figures (3-8A) and (3-9).

The co current flow set up was made from a simpler design of two inlets directed into an annulus channel at the chamber top cone, where the flow introduced from two inlets into a half circular closed copper pipes drilled with rows of 3 mm orifices. This annulus was packed with a fibre glass to create back pressure distributing the flow all over the groove before fed through perforated circular distributors illustrated in figures (3-8 B) and (3-10). The freezing unit designed to operated independently from other operations, spraying and fluidisation.



Figure 3-7: The design of gas mixer/vaporiser.



Figure 3- 8: The gas distributors inside the spray freezing chamber, A = for counter current flow, B = for co current flow.






Figure 3-10: The freezing medium flow in the co current spray freezing configuration.

#### 3.2.2 Spraying and atomisation

The spray measurement proposed in this research aims to obtain adequate sizing on the drops sizes that can be applied into developed spray freezing and drying model. The droplet size distribution is crucial factor in the adequate determination of the freezing and drying rates, the smaller the size distribution and narrow drop size range results in shorter freezing time of the particle sizes thence good heat and mass transfer prediction. The space limitation available in the spray freezing chamber that raise the question of the spray freezing space and distance available. These concerns set the criteria of the nozzles selection to a narrow coverage with a reasonable trajectory inside the chamber and good degree of atomisation homogeneity. The operation at low temperature may develop some complication of nozzle blockage and spray turbulence inside the spraying chamber, also the low temperature may affect the physical properties of the liquid feed that could hinder the degree of atomisation of spray.

An Investigation of Spray-Freezing & Spray-Freeze-Drying

There are three types of atomisers used widely in spray drying processes: pneumatic, hydraulic and rotary. Each one is particularly suitable for certain operations depending on the rig design and atomisation requirement (see chapter 2 section 2.2.2). In this research the atomisation requirements of (i) to atomise viscous liquids (ii) to a high degree of spray uniformity (iii) ability to operate at sub ambient temperature (iv) require a small chamber size. Three different nozzles had met the criteria indicated earlier, one of these nozzles is hydraulic and the other two pneumatic nozzle. These nozzles were supplied by BETE Ltd, Lewes, East Sussex UK.

## 3.2.2.1 XA Pr Pneumatic spray nozzle

The "XA pr" spray nozzle used in this research was a pressure round twin fluid (pneumatic) spray nozzle. It is an *internal mixing* twin fluid designed to produce fine and homogeneous spray with a narrow spraying cone (17-22°). It can also atomise viscous fluids. There are two assembly settings available for this nozzle, the "PR 050" and the "PR100". These differ in the diameter of the liquid feed orifice, which results in different atomisation behaviour and flow rate.

#### 3.2.2.2 SAM Pneumatic spray nozzle

This is also a twin fluid (pneumatic) spray nozzle. Its characteristic feature is the independent control of liquid and gas atomisation feeds for a highly refined control of drop generation and spray sizing. It is an *external mixing* nozzle, capable of spraying viscous liquids and slurries. It has a sophisticated design which allows it to produce cone spray or flat fan spray, which is determined by a pneumatic switch. Two assemblies are available for this nozzle "SAM-01-02" and "SAM-02-02", producing uniformly fine mist.

## 3.2.2.3 WL Hydraulic spray nozzle

The WL series are a full cone hydraulic spray nozzles, WL0.25 nozzle is suitable for small flow atomisation in a fill cone spray of 30° angle. It can also spray viscous solutions. The orifice in this nozzle is 1.09mm. The liquid flow rate feed into the nozzle is dependent on the pressure of the feed input.

	WL Series	XAPR series	SAM series
Models	0.253	Pr50 & Pr100	SAM 01-01 & SAM 01-02
Туре	Hydraulic	Twin fluid	Twin fluid
Spray Pattern	Full cone	Full Cone	Flat fan or full cone
Spraying angle	30°	12°-22°	Variable
Description of the drops in a spray	Coarse with wide distribution	Fine spraying and narrow distribution	Fine spraying and narrow distribution
Orifice sizes	Fixed	Interchangeable fluid & air caps	Interchangeable fluid & air caps
Atomisation gas feed	NA	Compressed nitrogen gas	Compressed nitrogen gas
Feeds mixing	NA	Internal	External

 Table 3- 1: Spray nozzle types and general descriptions (BETE Ltd).

# 3.2.3 Spray feed setup and operations

The two major concerns for the nozzle housing was that the liquid feed would not freeze inside the nozzle and that the position of the nozzle should be flexible and allows the PDA to measure the conditions at and below the spraying point.

The spray nozzle assembly was housed in an aluminium cylinder 700x100 mm which was held in place by a specially made collar through which it can slide to adjust the position of the spraying point inside the chamber. The cylinder also designed with interchangeable plates (for holding the nozzle centrally in place), which could be used with different types of nozzles. The empty nozzle housing cavity was initially filled with "Vermiculite" granules to insulate the nozzle, but was replaced with heated air jacketing surrounding the liquid feed line as illustrated in figure (3-11). This had led to better regulation and control of the nozzle body heater in addition to easing the process of nozzle cleaning and replacement. The nozzle body and atomiser feed temperatures were monitored during spray operations using "Type T" thermocouples (see section 3.3.3).

The feed connections to the hydraulic and pneumatic nozzles are shown in figure (3.12). The atomiser feeds were controlled from a switches near the base of the chamber. The atomisation gas were supplied from a compressed nitrogen gas cylinder in the range of 1-6 bar and the flow could be quickly turned on and off using solenoid valves. The pressure level was regulated using in-line pneumatic regulators. Twin fluid atomisers require a high ratio of gas to liquid feed amount (2:1 ratio) for sufficient drops disintegration to take place. Nitrogen gas was selected to be the suitable atomisation gas feed to keep a consistent gas composition (of nitrogen) inside the spraying chamber. The liquid feed initially transported from the feed reservoir into the spray nozzle using a triple diaphragm pump and controlling the pressure by varying the power supply to the pump. However as a results of a spray imaging experiments (see next section) this pump was replaced with a pressurised vessel.

The nozzle operation control panel was mounted 3 m away from the spray nozzle. The atomisation starts by on/off solenoid valves for gas feed and the liquid feed by manual ball valve, the flow rates regulated as feeds pressure. The pressure measurement was carried by a inline dial gauge read outs, positioned approximately 1 m a way from the spray nozzle. These appeared to lack sufficient sensitivity in order to control the feed pressures reproducibility and were replaced in later experiments with electronic pressure transducers (see chapter 5).







Figure 3-12: The spray nozzle connections, using a liquid feed pump.

#### 3.2.4 Spray imaging

Spray imaging experiments were preformed to initially assess the quantity of the spray formed and their stability. The spray operation was evaluated for stability and consistency. For this the "Planar laser light-sheet imaging" method was used. The spray was imaged by a single-digital-shot recorded with a PCO Sensicam Fast Shutter CCD Camera. The spray was illuminated the by back-lighting method using a EG&GMVS7020 Xenon flash unit. The image size was 1280x1024 pixels with 12 bit resolution intensity. The flash duration was 8 µs and the camera shutter speed was 1µs. The time of image capturing was set to 5 images per second for a duration of 15 images.

The images obtained from a number of spray-imaging test-trials had showed evidence of flow pulsation in the liquid feed which was likely to have been generated by the pump see figure (3-13). This could give rise to lack of reproducibility in the PDA spray characterisations measurements. The liquid feed pulsation results in variable pressures and flows through the

nozzle orifice that will affect the droplet atomisation giving variable results for the droplet size distribution and velocity measured by the PDA.

#### 3.2.5 Pressurised feeding system for spraying

The solution to the pulsation problem requires either flow pulsation dampers, or ideally a steady pressure vessel. Thus the triple diaphragm pump was replaced with a pressurised vessel providing a steady flow of the liquid feed into the spray nozzle. The liquid feed pressure was maintained from a "20 litres Millipore, UK" pressurised vessel, the pressure capacity of the vessel was 100 psi therefore the maximum liquid feed pressure obtained at the nozzle was 5.5 bar. Changing the compressed air pressure into the vessel regulated the liquid feed pressure. The atomisation gas used for the pneumatic nozzles was nitrogen gas from a compressed nitrogen cylinder. Due to the pressure drop in the feed line the feed pressure setting was based on a pressure measurement close to the spray nozzle, see figure (3-14).

The atomisation pressures were set prior to any spray testing to the desired conditions by having a trial spray and setting the regulating valves. The experiments were then preformed by opening and closing the relevant solenoid valves. At the end of the test all valves are shut off and the liquid atomised line flushed with pressurised nitrogen gas to empty any liquids and prevent the nozzles from freezing.



Figure 3- 13: Image sequence of water spray (1 bar gas & 1 bar liquid feeds) produced by XA Pr50 pneumatic nozzle.



Figure 3-14: Spray nozzles connection using a pressurised feed tank.

#### 3.2.6 Measurements and instrumentations

The temperatures and velocity of the freezing gas as well as the chamber temperatures were measured at selected points as follows, see figure (3-15),

- Supply of N<sub>2</sub> gas temperatures (T<sub>1</sub> and T<sub>2</sub>) were measured by PT100 multi purpose RTD probes, and the temperatures were displayed on a RS RTD temperature display (both ex RS components –UK).
- The liquid feed temperature (T<sub>L</sub>) measured by "Type T" thermocouple (ex RS components).
- Chamber wall (T<sub>w1</sub> and T<sub>w2</sub>) and nozzle body (T<sub>n</sub>) temperatures were measured by "Type T" adhesive thermocouples (ex Omega instruments). The temperature readings of these thermocouples were read from a Type T temperature display (ex RS components).

 The outlet gas velocity was measured by a hand held rotary vane anemometer (AIRFLOW LCA 6000 VAT) measured across a pipe 100 mm diameter. A number of readings were taken and the average value was calculated and used.



- $T_{1\&2}$  = the temperature of the freezing medium liquid and or gas temperature.
- $T_3$  = the freezing gas temperature at the spray point inside the chamber.
- $T_{4,5,\&6}$  = the freezing gas temperature in and out side the chamber.
- $T_N$  = the nozzle body temperature.
- $T_L$  = the atomised liquid feed temperature.
- $T_{w1 \& w2}$  = the chamber wall temperatures.
- Vel. = the measurement of the gas flow velocity out of the chamber.

Figure 3- 15: Spray freeze chamber instrumentation.

## 3.2.7 Spray freezing operation testing

## 3.2.7.1 Operation procedure of the counter-current spray freezing chamber

- 1. Connecting the nozzle and securing it tightly in place.
- 2. Mounting all glass windows and closing them tightly.

- Purging the chamber with compressed nitrogen gas from a cylinder for a period of 18-20 minutes.
- 4. Introducing liquid nitrogen into the vaporiser vessel and keeping one feed of the 4 inlet manifold open to cool down all parts gradually with sub-ambient nitrogen gas, for 3-5 minutes.
- 5. Increasing the flow of  $LN_2$  through the inlets (at least two at each time), depending on the temperature of operation desired.

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6. Finally commencing spray as pre-set.

This first testing operation of the spray freezing chamber indicated a number of problems in the design and operation of the constructed chamber, the first observation of this problem was the poor strength of the chamber wall metal which was not strong enough to withstand the heat of welding during construction. This resulted in a series of problematic operational faults and difficulties in operation and control

- There was a problem of air leaks into the system from different places, namely windows, the spray nozzle-holding collar, and other chamber joints, poor gas-kitting of the joints exasperated contraction during cooling. The humidity level present in this leaked stream condenses at low temperatures in the chamber and created a white mist that reduced visibility inside the chamber, which was unacceptable for the spray characterisation analysis.
- The slow cooling power of the gaseous medium in the counter-current operation of the freezing chamber set up.
- The freezing gas pools in the lower section of the spraying chamber due to the high density of the gas creates temperature gradients between the spraying region and the freezing medium inlet region.
- The spray nozzle freezing (blockage) during operations, and one spraying run managed each time. The blockage is caused by the freeze of the liquid feed inside the pipe feeding the atomiser, even though the pipe is placed in insulated vessel.
- Spray turbulence and misting inside the chamber that's inhibits the vision, which could be caused by

- - The gas flow turbulence inside the chamber resulted from uncontrolled freezing gas input, the flow volume vary with the temperature of the gas.
  - Turbulence of the spray freezing gas due to wide dimension of the spraying chamber construction.
  - Temperature gradient difference in the gas stream of the spray freezing chamber enhanced the buoyancy force to carryover the spray particulate close to the wall in an upward direction, thence creating a dense cloud of spray particulate.
  - The small size of the spray / particulate (fine spray).

The solutions to some of these problems were easy to tackle, such as the sealing the leaking gaps in the joints of the chamber and the windows. While others require serious operational set up changes for example the temperature gradient of the gas and turbulence. But the problem of primary concern in this configuration operation was the sub-ambient gas pooling in the chamber, as it may cool the drops in the spraying zone but not to the freezing level that could cause snow flak or agglomeration of the particles in the cooler regions down stream the chamber. In addition to difficulty of controlling the gas extraction flow to maintain a balance of eth spray settling and carry over. Therefore it was decided to switch the spraying operation to a co-current configuration due to the simplification of the operation and modelling of the process.

# **3.2.7.2** Operation procedure of the co-current spray freezing chamber

The difficulty of spray entrainment was anticipated in the initial design especially since the ASFD system is a newly developed technique that is subjected to trial and error planning, and the operation test were most influential elements in the design. The conversion of the chamber operation system was taken into consideration in the draft of the design with few alteration to the chamber (see section 3.2.2). Thence it was possible to divert the freezing medium (the spray operation mode) input and output into a reverse order by first removing the inlet distributor at the lower end of the chamber and placing an alternative distributor at the top of the chamber. The operation procedure of this configuration mode

1. Carrying the steps 1-4 of the previous section.

- 2. Increasing the flow of  $LN_2$  nitrogen to higher value so cooling the chamber by direct rain of  $LN_2$  to accelerate the chamber cooling from ambient temperature due to the mass of the chamber and its large heat load.
- 3. Then reducing the flow till maintaining the spray freezing temperature of operation desired, and the wall temperature of the chamber is ±5 °C. The gas flow velocity maintained by adjusting the extraction power of ventilation line.
- 4. Finally commencing the spray freezing at the pre-set conditions.

An operational problem solving tasks and investigations was carried to improve the chamber performance by rectifying the problems encountered in the previous section. Here the misting within the chamber operation was less than that of the counter current system.

## 3.2.7.3 Problem solving of the occurred problems

The operation of co-current configuration of spray freezing was commenced after making more effort to seal spotted air leaking gaps of the windows and other joints in the chamber.

The spray was fine and the temperature control was less difficult, however spray clouding was the first reported feature of this spraying operation. This may be caused a turbulence that be caused by non-uniform gas flow in the chamber resulting in a chaotic drops (motion especially closer into the wall and the widows). This cloud reduce the visibility of the spray in the chamber. The use of higher gas extraction and increasing the floe of the freezing medium helped clearing the visual inhibition inside the chamber.

The frozen spray mostly adhered to the metal of the lower conical section in the chamber, this may be reasoned to either incompatibility of the cooling power with the atomisation capacity or the particles melting when contacting the chamber wall (not cold enough) or finally due to the wall roughness and degree of cone inclination of the chamber wall. It is better to cool the walls of the chamber (metal) to a lower temperature than that of the spray freezing operation. This even helps preventing the particulate (spray frozen) from sticking to the walls of the chamber, continue cooling the chamber with  $LN_2$  flow till the wall metal temperature reach 5

<sup>o</sup>C below the spray freezing point temperature. An Investigation of Spray-Freezing & Spray-Freeze-Drying Nozzle freezing problem was solved by attaching an electrical heating elements to the nozzle body. Usually the nozzle freezes due to liquid remaining inside the nozzle and or the pipes leading to it, therefore liquid feed lined were connected to a purging pressurised nitrogen line to evict any liquid remaining in addition o jacketing the liquid feed line leading to the nozzle body with a heated air line as illustrated in figure (3-11) and (3-12).

The encountered problems were reported in different aspects and operations of the spray freezing process, nozzle blockages, external humid air leak into the system, spray turbulence inside the spray freezing space hence visual inhibition of the spray pattern. The solutions of these problems were assessed individually and based on the experimental observation and analysis of the conditions and causes with regards to the overall process, these problems then solved separately as described below

## 3.2.7.4 Spray misting and entrainment reduction

Spray entrainment control is crucial measure to create sufficient visual field suitable for the LDA/PDA analysis. The entrainment presence is a turbulence factor, although it may a positive feature for the heat transfer operation and freezing, but it inhibits a clear of the spray or particulate visualisation that's obstruct or reduce the sensitivity resist of the spray analysis (characterisation). Some concepts were used to reduce this spray turbulence such as using mesh screen to capture the spray and reducing the spray or droplets circulating inside the chamber, while the freezing gas exhausted through mesh into the outlet vent. However it was false practice as the build of the ice particles on the mesh screen created a pressure drop and starts turbulent again, see figure 3-14.

The second solution tried was the of a draining funnel to direct the spray before turbulence start appearing at the point where it loses inertia moment, this practice is used in the PDA measurement. The cone placed at a distance close enough to provide a free trajectory for the spray analysis by PDA, 50 cm below the spraying point. The cone presence fulfilled it promise of directing the spray down war when it was liquid, however due the solidification the spray tend to bounce back up ward and the drain outlet clogged quick enough with out providing sufficient length of spray stability.



Figure 3-16: Spray entrainment elimination by a trapping on mesh and draining funnel inside the chamber.

The obtained results from these trials was not of high efficiency of lowering the turbulence for good time duration of 30 seconds, therefore none was applied and chamber is operated thereafter in its current format with out any spray capturing tools. Thence stable spray for up to 10 seconds duration was accepted for the PDA characterisation measurements.

## 3.3 Spray freeze-drying rig

The operation requirement of this rig design can be summarised by " production of a fully frozen particles forwarded in into a fluidised bed where it would be dried by sublimation under atmospheric or lower pressure and sub-ambient temperatures". The process will operate in a batch circulating closed loop of freeze-drying. The time duration and critical control of the process operation conditions requirement dictate a continuous monitoring the changes to the temperature, flow, pressure and humidity. These conditions can be inter-related, i.e. change in one will influence the other in chain reaction, the operation is anticipated to run for a significant time it will be monitored using data acquisition recording of these parameters atomised accordingly.

## 3.3.1 Spray freezing chamber

The spray freezing chamber constructed for the spray characterisation experimentation had significant success in spray freezing operation as noted from the frozen particles collected in the product separation of the box. Therefore the same rig was used for the spray freeze-drying process in the co-current configuration.

## 3.3.2 Particle-gas separation cyclone

The frozen particulates produced in the spray freezing chamber were carried out by a large volume of gas from which they need to be separated without compacting together. The use of a cyclone can give good separation and flow continuity, whilst the particulates settle in the bed vessel under their terminal velocities.

A stainless steel cyclone was purchased from Rigal-Bennett Group, Goole, East Yorkshire UK. The cyclone sizing and efficiency was made based on particle size from the PDA measurements. The calculation indicated 80% minimum efficiency of separating (75 m<sup>3</sup>s<sup>-1</sup>) gas-particle flow rate, produced in the spray freezing chamber when spraying in 1.5 ms<sup>-1</sup> flowing gas assuming a particle size of 10  $\mu$ m.

## 3.3.3 Freeze-drying gas supply

The freezing and drying medium used for this chamber design was a mixture of vaporised liquid nitrogen and cylinder nitrogen gas from the same source as used in the spray freezing chamber but using an independent feed. The freezing medium (liquid or nitrogen gas) is atomised in centrally inside a 6" ID stainless steel pipe allowing the flow fully develop and distribute across the bed section area.

The flow plan described in figure (3-17) begins by the opening of the  $LN_2$  flow from the dewer through a ball valve, the feed is initially pressurise 2-3 bar forced into the expansion tank at atmospheric pressure through 4 mm orifice. The flow is then mixed with ambient temperature nitrogen gas that provides vaporisation latent heat, when required. During the spray freezing and drying operation the gas expansion tank may be flooded with liquid nitrogen that is flown under the gravitational force and driven by the level head through the lower outlet of the tank into the supply for the fluidisation freeze-drying. Also a separate pressurised nitrogen gas provides the freeze-drying gas line with the pressure and temperature required fore operation.



Figure 3-17: Freezing medium flow in the spray freeze-drying chamber.

#### 3.3.3.1 Calculation of freeze-drying gas flow requirement

The gas unit in the freeze-drying rig will essentially consist of a mixture of nitrogen gas and water vapour. These components can be characterized by the partial pressures within an overall mixture pressure in a constant volume. The partial pressure  $(P_v)$  of the water vapour in the air cannot increase beyond a certain limits. This limit is the saturation partial pressure  $(P_{vs})$ , the value of which depends on gas temperature. So at a low temperature a rather low (absolute) humidity causes a high relative humidity and visa versa. In practice mass transfer limitation within the fluid bed will mean that the saturation partial pressure will never be reached, but it allows an upper limit to be specified.

The freezing modelling requirement using the liquid nitrogen can be calculated using the medium (gas or liquid) nitrogen thermal properties from the available literature, and the volume flow can be calculated from the ideal gas law

$$PV = nRT Eq (3-1)$$

Where vessel volume (V) and overall system pressure (P) filled with nitrogen mixture of nitrogen gas and liquid here (n) is the quantity of moles of gas per and vapour, (R) is the ideal gas constant 8.3145  $\text{Jmol}^{-1}\text{K}^{-1}$ , and (T) is the temperature in Kelvin.

The gas pressure and volume in the atmosphere can then be considered as two-component gas mixture of dry nitrogen and water vapour according to Dalton's law.

The partial pressure of each component can be calculated using the ideal gas equation using the (n) as the number of moles for each component in the mixture. The saturation vapour pressure of water can be estimated from correlations, and it is different depending on whether the vapour is in equilibrium with liquid water or ice as seen in equations (3-3 and 3-4) if the temperature expressed in degree centigrade.

$$p_{vs_{(over liquid)}} = 610.78 \times \exp\left(\frac{T}{T + 238.3} \times 17.2694\right)$$
 Eq (3-3)

$$p_{vs_{(over ice)}} = \exp\left(\frac{-6140.4}{T + 273.15} + 28.916\right)$$
 Eq (3-4)

In drying a useful quantity to define is the relative humidity of the gas defined as

$$RH = \frac{P_{\nu}}{P_{\nu s}}$$
 Eq (3-5)

The relative humidity values are generally expressed as a percentage and indicate the ability of the gas to dry. Other term involved is the absolute humidity ( $\omega$ ), which is the ratio of water vapour ( $m_v$ ) to the dry gas ( $m_g$ ) masses in the stream

$$\omega = \frac{m_v}{m_g}$$
 Eq (3-6)

The drying gas stream has maximum capacity of water vapour at any temperature, and the vapour condenses if the absolute humidity increases and exceed the saturation value. During freezing or cooling the originally unsaturated air's relative humidity starts to increase and the absolute humidity with it, the partial pressure of vapour, remain unaltered, but both tend toward the saturation values. At RH = 100% the temperature is known as the **dew-point** ( $T_d$ ) temperatures, which is defined as the temperature upon further cooling the gas becomes saturated and begin to condense. In the very low temperature cases frost-point ( $T_f$ ) temperature is used where ice is formed at the saturation point of the gas rather than liquid condensate. At the dew point temperature The environmental vapour pressure is the saturation vapour pressure

Water vapour pressure is not only dependent on the amount of water it is also (very slightly) influenced by the presence of gas in the container. The heat content, usually called the *enthalpy* (kJ/kg), of gas rises with increasing water content. This hidden heat, called latent heat by air conditioning engineers, has to be supplied or removed in order to change the relative humidity of air because it will require evaporation or condensation of water. The transfer of heat from an air stream to a wet surface, which releases water vapour to the air stream at the same time as it cools it, is the basis for psychrometry and many other microclimatic phenomena (Pruppacher Hans *et al.* 1997).

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## 3.3.3.2 Freezing-drying gas flow requirement-typical conditions

If a (250 g) batch of a concentrate with solid content of 30.7% (wet basis) is dried to 99% (wet basis) this will correspond to a mass of water 173.25 g. Using the ideal gas law if this water mass vaporised to form a saturated vapour it would occupy a volume of 3631.7 m<sup>3</sup>. This volume is independent of the amount of nitrogen gas. The following table (3-2) shows the volume of gas that must be removed at each temperature (assuming saturation condition).

Table 3-2:	Water vapour pressure and volume at different temperatures calculated from ideal
	zas law

Temperature (°C)	Saturation vapour pressure $P_{\nu s}$ (Pa)	Water vapour volume per (100 g)
0	623.93	20.21
-5	410.29	30.17
-10	265.54	45.75
-15	168.99	70.52
-20	105.64	110.63
-25	64.80	176.79
-30	38.96	288.15
-35	22.93	479.57
-40	13.19	816.17
-45	7.40	1422.43
-50	4.05	2542.76

## 3.3.4 Fluidisation freeze-drier

## 3.3.4.1 Fluidisation

The major reason for adopting the fluidised bed system is to improve sublimation rates as a result of high heat and mass transfer coefficients. The fluidised bed accommodates the main function of the process freeze-drying system, sublimation of ice from the frozen suspended particles. Where mass transfer driving force is the solvent partial pressure gradient between the drying nitrogen gas and the solid particles. The particles collision in the fluidisation will be critical in the acceleration of the mss transfer, by refreshing the boundary layer

surrounding the particles. The fluidisation freeze-drying is possible to operate at low pressure therefore the vessel should be designed and constructed to suit the low-pressure operation by being leak proof vessel. In a similar concern to the leak minimisation the vessel should have a minimum level of intrusive measurements.

The fluidisation operation required for this freeze-drying research is "An operational unit capable of holding and subliming known water mass ice particulate without losing the particle structure integrity to melting by freezing and drying the batch in controlled temperature and pressure".

The low vapour removal capacity of the drying gas at subzero temperatures means a requirement for a large volume of freeze-drying gas to remove a small mass of water (section 3.3.3.2) and maintaining freezing simultaneously. If is preformed at atmospheric pressure the particles would be expelled from the bed by the high drag forces of the gas through the bed, and need to be recovered in a filter bag as found by Leunberger et al (1991). This practice could result in product quality loss, and does not make use of the fluidised bed.

The alternative approach is to operate at lower overall pressure can help reducing the gas density and viscosity which reduces the drag and pressure forces on the particles, the conditions can thus be turned to those favouring "bubbling fluidisation" near the upper layer of the bed. Kusakabe et al (1989) reported that low pressure fluidisation regimes a shallow bed otherwise the upper part of the bed fluidises while the rest remains quiescent (Kusakabe *et al.* 1989). Lowering the pressure would also increase the molecular mean free path of the gas by reducing the volume of the gas in system at a time, the mass transfer rate capacity not affected by this if not enhanced since transfer is temperature dependent and affected by eth pressure gradient.

Since the freeze-drying gas volume requirement is high, low pressure application can help lowering the vacuum load requirement by reducing the mass of gas within the system and hence reduce the cooling requirement of the gas. In the partial vacuum or low pressure operations the gas thermal conductivity increases in comparison to that of vacuum operations.

An Investigation of Spray-Freezing & Spray-Freeze-Drying

One of the disadvantages of vacuum freeze-drying operation is the low thermal conductivity of the gas in the chamber resulting in slow heat transfer (Mellor 1978). Increasing the operation pressure in a cyclic operation or partial vacuum help increasing the gas thermal conductivity within the freeze-drying system hence accelerating the mass transfer rate (King *et al.* 1968, Mellor 1978).

The frozen particulate produced by the spray freezing was considered to be in the group A and or B class of Geldart scale, their behaviour in vacuum fluidisation should also be considered. Low pressure fluidisation (at pressures below 0.005) (Germain *et al.* 1976). It typically involves a laminar flow regime, which is different from that of the atmospheric system, however the hydrodynamic behaviour of fluidised particles shows bubbling and onset fluidisation is similar to that of the atmospheric pressure. The conventional fluidisation equations of are not applicable at low pressure but it is known that reducing the pressure increases the minimum fluidisation velocity. The mass transfer of a particulate material in fluidised bed depends on vapour diffusion through the boundary film on the particle surface and is therefore affected by the operating pressure condition. Yamamoto et al (1980) reported that fluidisation under reduced pressure would have no significant effect on the heat transfer coefficient while the mass transfer increases, this may be explained by the reduction the gas thermal conductivity than that of atmospheric pressure (Yamamoto *et al.* 1980). Casal et al (2002) presented formulation for the low pressure fluidisation heat and mass transfer as well as the flow dynamics of drier (Kozanoglu *et al.* 2002), described in chapter 2 section 2.3.3.

It was planned to freeze-dry a 250 g batch of frozen concentrated liquid containing up to 70% water of which 99% is removed by sublimation. This results in the following sample quantities

- $X_T = 250$  g, total sample mass
- $X_{w0} = 175$  g, is the total water present in the batch (70%)
- $X_{wf} = 1.75$  g, is the final moisture content in the dried batch (1%)
- $X_{wr} = 173.25$  g, is the mass of water removed from the sample as sublimed vapour
- $X_f = 76.75$  g, is the mass of the dried sample (99% dried)

The mass was chosen as a compromise between allowing online measurement of sample mass and amount of water to be removed to an acceptable level.

#### 3.3.4.2 Vessel design

The possibility of a low-pressure operation for the fluid bed would make construction of a spraying chamber integrated with a fluidised bed a difficult task. Therefore it was decided to have a separate and relatively small fluidisation chamber. Thus in the recommended design, the spray frozen particles are separated from the gas stream by a cyclone and forwarded to an attached fluidised bed.

The use of sub-ambient processes in this system needs a great attention to details when design and sizing the vessel, not least its connections into other process operation units, sprayfreezing chamber and the gas circulating and cooling system. The important requirement in this vessel design is the integrity and leak proofing of the inside volume of the vessel from the surrounding atmosphere.

The main outer vessel is constructed from 316 stainless steel material to with stand low pressure operations and houses inner fluidisation unit. A diagram of the vessel is showing in figure (3-18). The volume of the vessel is  $0.022 \text{ m}^3$  attached at the lower end with an up-flow freeze-drying gas inlet of 0.15 m diameter inner. The flow leaves the fluidisation vessel from two side outlets 0.0754 m diameter each. It is provided with two view ports for monitoring the process flow operation. It is connected to the cyclone separator via a vacuum sealed butter fly valve to feed the frozen particulate into the fluidisation unit. This is a 0.164 m inner diameter and 0.17 m long poly carbonate cylinder fitted at the lower end with 3 mm thick stainless steel sintered mesh. This forms a shallow bed of 2 cm high for a batch of 250g of 50  $\mu$ m coffee powder. The poly carbonate tube sits on a specially constructed annular load cell to enable on-line measurement of the sample weight. This is described in detail in later section. After felling the bed the butter fly valve would be shut, the spray chamber would be disconnected and the fluidisation commences.

For a heterogeneous Fluidised bed it is more practical to calculate the entrainment velocity for the whole range of particles in the bed in order to achieve safe fluidisation operation with minimum loss. The sublimation-fluidised bed is a dense phase process. The design of the fluidisation vessel is an advisable to have significant disengagement space to trap any carried over fines (Richardson *et al.* 2002).

The freezing-drying  $N_2$  gas introduced into the fluidised bed from an atomiser at the a distance at least 1.5 m away from the inlet into the fluidisation cylinder. This gas flow rate and temperature are controlled from the variation of  $LN_2$  to  $N_2$  flow ratio. The outlet ga sfrom the fluid bed passes through a filter curtain covering the inner wall of the fluidisation cylinder into 5 mm holes 1 cm apart (the holes stretch along the circumference and from the top till the 10 cm distance above the bed upper layer), and then leave the vessel via the two outlets into vapour trap by the suction of the vacuum or the circulating fan (see next section).

#### 3.3.4.3 Vacuum operation

The available vacuum pump is rotary vane oil sealed Werner Rietschle-Germany model CLF100. It has an operating capacity of 100m<sup>3</sup>hr to 10 Pa. The calculations made in previous section indicates the requirements of 400 m<sup>3</sup> per hour to complete the mass transfer by freezedrying in one hour time in gas saturation relative humidity of 50%. Thus this pump at 100% operation performance needs minimum of 4 hours to complete the freeze-drying operation. Therefore it was decided to have a secondary ancillary fan inline to aid gas removal and pressure maintenance.



Figure 3-18: Sketch of the fluidisation vessel.

#### 3.3.4.4 Freeze-drying gas dehumidification

To reduce the load on the vacuum pump a system of drying and re-circulating gas was incorporated into the process.

There are number of gas drying methods the most common used in freeze-drying processing is a refrigerating condenser. Though, in the current design the temperature control is critical during operation. Having a condenser coil inside or near the fluidisation vessel may create a complication of temperature control, in addition to the excess requirement of liquid nitrogen for cooling power. Therefore gas drying by adsorption was chosen as it involves a passage of vapour on inert adsorbing surfaces.

Adsorption is a physical-chemical separation technique that is an effective removing and/or recovering technique for trace components from a flowing feed or process effluent stream. The most common adsorbent used in industrial and laboratory scale adsorption drying processes are Activated Alumina, Molecular sieves, and silica gels. These are characterized by high porosity and adsorption surface area as well as an affinity to water binding due to their hydrophilic, polar nature. The rate of transfer is known to be proportionally related with the system total pressure and inversely proportional to its temperature.

The adsorption air drier is an enclosed bed of inert desiccants, which require periodic regeneration. The ability of the bed to dry the gas stream will depend on the increase in temperature of the gas between the fluid bed and the dryer, but this is anticipated to be low.





The gas drying system proposed for the SFD system is a fixed bed cartridge of 4-5 mesh hygroscopic "zeolite 4A" beads (ex Acros Chemicals, UK) which has a good adsorption performance at temperatures below 0 °C, in comparison to other desiccants (Zhukova *et al.* 1962). This can be followed by a layer of silica gel granules, which changes colour depending on their moisture content to act as an indicator of the state of the bed. The amount of adsorbent required packing was estimated on the bases of having a pack size suitable to twice the capacity to completely remove the water vapour from the freeze-drying gas.

The "Zeolite 4A" Packing is filled inside the flexible reinforced PVC pipe with a total length of 900 mm and 80.8 mm ID. the packing is held in place by a filter mesh preventing it from falling between the two vessels. For and granule adsorbent with a diameter minimum of 3 mm, bulk density of 660 kg/m<sup>3</sup> and adsorptive capacity (50% RH @ 25 °C) = 210 mg/g. The possible adsorbent packing required is then to adsorb 173.25 of water vapour (twice) is 1.65 kg, this has a volume of 0.0025 m<sup>3</sup>. There was easily free space available in the PVC tube lines to accommodate these mass of packing.

# 3.3.4.5 Circulation system

The desiccated gas would be circulated by an axial fan (CMR Controls, Essex UK) located after the point of union of the two desiccation lines from the vessel outlet and the vacuum line inlet. This re-circulate gas not passing to the vacuum pump back into the fluidisation freeze-drier.

The fan was placed in a specially constructed housing suitable for low pressure operation and the flow was regulated from the electrical input into the fan. The fan could be isolated from the circulation line by a butter-fly vacuum sealed valve, see figure (3-19). Down stream is was an 150 mm ID stainless steel elbow at the centre of which the cooling freezing medium is introduced and the flow was then directed into the fluidised bed and circulating onward.

# 3.3.4.6 Measurement instrumentation

The spray freeze-drying process will operate in an integrated functionality that requires overall process measurements and characteristic to each operation separately be monitored



Figure 3- 20: Freeze-drying operation.

These parameters are pressure, temperature, humidity, and flow rate (calculated from flow pressure and temperature measurements). They are separated into two categories according to their relevance to the operation influence on the product characteristics. The first category was for monitoring purposes only and included the nozzle body temperature, the spray freezing chamber wall temperatures, and cyclone temperatures. The second category included temperature, humidity, pressure, and flow measurements around the fluidised bed, and the temperature at the spraying point the spray freezing gas flow. This second category were also important for analysing the process and process modelling. Therefore the first category was monitored on data displays , while the second data collection was logged from a data acquisition hardware into a PC for the duration of operation.

The measured parameters and locations are indicated in figure (3-20). The probes used in these measurements are Type T thermocouples and PT100 thermal resistance probes for temperature measurements. Gas flow rate is measured volumetrically using a venturi tube ,specially made from a stainless steel billet (FMC Measurement Solutions, Norfolk, UK) for the spray freezing chamber flow input and an averaging pitot tube (ex Omega, UK) for the fluidisation vessel. The flow humidity sensor was a capacitance electronic transducer (ex. Michell Instruments UK). The data acquisition hard ware is a Data Scan 7321 and 7050 having a total of 16 channels linked into PC and was operated using DasyLab software.

The measured parameters logged onto the PC were sub-divided between two operations, the first is spray freezing;

- $T_1$  = Initial temperature of the chamber flow (liquid nitrogen or nitrogen gas).
- $P_1, P_2 =$  Flow pressure in a  $\frac{1}{2}$ " ID pipe and across the venture orifice.
- $T_{sp}$  = The chamber gas temperature at the spraying point.
- $T_{cy}$  = The cyclone gas temperature.

The second operation parameters were

- $T_2$  = Initial temperature of the dry fluidisation flow.
- $T_3$  = The temperature of partially saturated gas at the fluidised bed outlet.
- $T_4$  = The temperature of the freeze-dried particles in the bed.
- $T_5$  = The temperature of the sintered mesh.
- $H_1$  = Initial humidity of the drying gas flow.
- $H_2$  = Humidity of the drying gas at the outlet.
- $\Delta P$  = Pressure drop of fluidisation gas flow, used to measure the flow rate.
- $P_3$  = The pressure of the fluidisation system.

The chamber gas flow and the fluidisation flows of the process were calculated using standard equations of flow through a venturi and across an averaging pitot tube for the specific dimensions of the rigs using the  $P_1$ ,  $P_2$ , and  $\Delta P$ .



Figure 3- 21: The instrumentation of the overall spray freeze-drying process, the schematic figure shows the parameters logged into the PC by DasyLab.

#### 3.3.4.7 Rate of freeze-drying determination

It is a necessity of the study any drying process to obtain a representative reading of the moisture loss from the dried material as time proceed. There is a choice of moisture loss measurement method, each with characteristic features that are useful for certain process measurement. The most common measure method is an intrusive type whereby a sample is periodically collected and its moisture content determined. This would have caused problem for a system operating under vacuum. Therefore the selected method was to have an in situ method of mass transfer measurement. The solution suggested was a novel weighing system, where the processed sample mass is measured with time enabling the varying parameter of moisture loss by sublimation to be assessed.

The proposed design entail a possibility of measuring the bulk moisture loss with time if the fluidisation vessel is mounted on a flexible shelf of a carefully selected material. The bending strain can then be measured and calibrated against the sample weight. The shelf design proposed is a spring disc, which should operate within elastic range, so that bending caused by the sample is recovered once the weight is removed with no permanent damage. The bending strain is measured using 8 strain gauges arranged as indicated in figure (3-22), they are connected in a full Wheatstone bridge. The voltage signals generated from this bridge are calibrated against a predetermined mass change, then the data are fed into the PC via the data acquisition device. These signals are converted into weight changes by the DasyLab software.



Figure 3- 22: The strain gauge assembly and connection

The strain gauges used in this design where supplied and bounded by Vishay Nobel Measurement UK.

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#### 3.3.4.7.1 Design of the spring disc system

The principle of weighing system measurement from the strain measurement is described first for a cantilever operation; The strain gauge responds to a strain by changing its electrical resistance according to a linear relationship.

$$K\varepsilon = \frac{\Delta R}{R}$$
 Eq (3-7)

Where

 $\varepsilon$  = the strain,

 $R \& \Delta R$  = the resistances and the change in the resistance respectively,  $L \& \Delta L$  = original length or distance and the change in the length respectively, K = is a gauge factor constant.

Therefore, resistance changes of the gauge can be used as an indicator of the strain,

For a Hooke's Law material

Where the stress ( $\sigma$ ) is the ratio of the loading force to the sectional area of the under stress is directly related to strain ( $\varepsilon$ ). (*E*) is the constant of proportion and is known as the modulus of elasticity, which depends on the material. (*F*) is the loading force and A is the cross vertical planner cross sectional area of the specimen under load. Stress results in a fractional change in length or volume, defined as strain. Hooke's law states that stress is directly proportional to strain, but ONLY up to a limit called the yield stress. If the material in question exhibits linear-elastic behaviour, and Hooke's law applies, then a linear variation of normal strain may be assumed to occur during bending. Bending stress is the normal stress that is induced at a point in a body subjected to loads that cause it to bend. In the case of bending a spring dick there is no change in overall length, but there is a change in the length of the upper and lower surfaces; considering Cartesian co-ordinates as in the figure below, the disc will bend when it is subjected to a tensile load, therefore the equation for bending stress is used and is given as

$$\frac{\sigma}{y} = \frac{M}{I} = \frac{E}{H}$$
 Eq (3-10)

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Where	М	= the bending moment at the gauge location,
	у	= the distance from the neutral axis to the straight disc top surface (half of the thickness of the strip),
	Ι	= the sectional modulus which depends on the geometry of the cross section,
	Ε	= the Young's modulus of the material (stainless steel),
	H	= the force at the counter side of the moments.

The spring design bending strain and stress calculations are more complicated than that of the cantilever and so the equations presented in appendix I, the formulations used in this calculations obtained from (Benham *et al.* 1987, Young 1989). The device were calibrated at ambient temperature and pressure for mass up to 300 grams and the result detected was readable by the data acquisition hardware. The operation under sub ambient temperature and pressure the disc was not subjected to pressure and temperature difference with ambient conditions.







Figure 3- 24: The spring displacement.



Figure 3- 25: Calibration line of the designed spring disc, at ambient temperature and pressure.

## 3.3.5 Spray freeze-drying chamber operation

The chamber is at ambient temperature before operation, and requires purging and cooling before the operation. The system is composed of three separate main units: spray freezing chamber, cyclone separator, and finally the freeze-drying chamber. The first two units operate at low temperature and at atmospheric pressure where as the fluidisation vessel is operated independently, for a longer duration and at different operational temperature and pressure. As the spring disc and other sensors is not suitable for a very low (cryogenic) temperatures, the purging and cooling of the fluidised bed is dealt with separately to the rest of the system.

# 3.3.5.1 Purging the system

## 3.3.5.1.1 The spray freezing chamber and cyclone

The fluidised bed is isolated by closing the butterfly valve between the cyclone and the fluidised bed. The spray-freezing chamber is then purged with nitrogen gas from a cylinder for a period of 5 minutes at flow pressure of 5 bars. Liquid nitrogen is the introduced to gently cool and purge the chamber from ambient temperature until it reaches (non freezing) cold temperatures (0 to 5 °C) gas temperature in both the spraying chamber and the cyclone, during which time the nitrogen gas from the cylinder is turned off. The exhausted gas is forwarded from the cyclone to the extracting duct.

## 3.3.5.1.2 The Fluidised bed

- 1. The vacuum regulating valve from the pump, and both butterfly valves between the fan and the cyclone are closed.
- 2. The vacuum pump is turned on. The vacuum-regulating valve is open to evict the air from the chamber.
- 3. When nearly full vacuum is reached the vacuum regulating valve is closed and the chamber filled with ambient nitrogen gas from the cylinder, until the pressure reaches atmospheric.
- 4. Repeat stages 2 and 3, but using liquid nitrogen instead of cylinder nitrogen to purge and gently cool the chamber to chilled temperatures.
- 5. Repeating stage 4 twice if necessary.

## 3.3.5.2 Cooling the system

## **3.3.5.2.1** The spray freezing chamber and the cyclone

Allow liquid nitrogen to flow into the spray freezing chamber for rapid cooling of the metals of the chamber to the spraying point temperatures or below. The excess of the liquid nitrogen that may rain inside the spray-freezing chamber will drain to the cyclone and cool the cyclone at the same time. It is important to have the wall temperatures of the cyclone and the spraying chamber below the freezing point the temperature of operations.

## 3.3.5.2.2 The fluidised bed

Keeping the butter fly values of the circulating gas in the fluidised bed closed, while the value between the cyclone and the fluidised bed open. The feed of liquid nitrogen was opened into the chamber and the fluidisation vessel to cool it to the operation temperature desired, here the vacuum pump acting as suction unit of the freezing gas from the cyclone as well as the fluidised bed. The system is then open to atmospheric pressure, for a few minutes till cooling the chamber metals to  $-40^{\circ}$ . Then reducing the flow till maintaining the temperature the gas inside the fluidised bed to that of operation conditions.

Note that the temperature of the circulating gas should never drop below a temperature of  $(-50 \,^{\circ}\text{C})$  as the humidity and pressure sensors are damaged below these temperatures. Also care must be taken that the exhaust gas outlet from the cyclone is extracted and that there is no back feed to the system from atmospheric air (the air will be humid and cause problems). After stabilising the temperature of the gas and metals walls of the chamber to temperature of adequate spray freezing, spray freezing may commence.

# 3.3.5.3 Operating the spray freeze-drying process

After the spray freezing temperature is reached the spraying operation was commenced at preset atomisation pressure foe the specific nozzle, as described in section 3.2. The fluidisation freeze-drying carried as follow

- The settling particle falling into the fluidisation vessel forming a bed, which was slightly aerated by an upward flowing gas through the sintered mesh to prevent them from compacting and keeping tem frozen at atmospheric pressure.
- Once the bed was filled with a 250g batch (monitored from the spring disc bending), the butter fly valve between the cyclone and the fluidisation vessel was closed.
- Thence the vessel evicted by opening the vacuum regulating valve to the desired pressure and introducing the freeze-drying medium required to maintain the operating temperature and flow.
- Monitoring the sample weight change with time till the drying process was completed.



Figure 3- 26: The overall spray freeze-drying process.
# 3.3.5.4 Problems of the spray freezing rig operation

# 3.3.5.4.1 Vacuum fluidized bed

There were number of problems during the operation of this low pressure fluidization unit,

- The operation of the vacuum fluidized bed reported some problems with the atmospheric leak into the system that required to checking the bolts tightening before spray freezing operation.
- The spring material was selected (0.1 mm thick) for operations of a low gas flow, and this was not the case by using 100 m<sup>3</sup>/hr vacuum pump, which lead to the deformation of the disc and shifting of the strain gauge off-setting. Therefore this drying kinetic measuring device was placed on hold in the current research.
- The stainless steel sintered mesh attached to the fluidisation compartment was densely packed material that created resistance to the gas flow to the bed. It was thought that it played a possible role in deforming the spring disc. Therefore it was replaced with a micron sizes mesh wire supported on a porous plate and attached to the fluidisation compartment via an holding ring. Due to this difficulties the testing of fluidisation trial was not carried out in this rig operation.

# 3.3.5.4.2 Cyclone operation

The cyclone cooling was an imperfect when connecting the butter fly valve with the vacuum vessel is shut, and leaving the lower part of the cyclone at temperatures than sub-ambient due to the dead end caused by the closed butter fly valve, which was risk of melting the particles as the forwarded to the fluidized bed. Therefore, it one stage of the fluidization vessel cooling the flow was directed upward through the butter-fly valve into the cyclone.

It was also noticed that the ventilation power of the exhausted gas from the cyclone was high to carry most of the spray frozen particles out of the system without allowing the separation to take place. This required ventilation power adjustment by either having no extracting ventilation or placing a flow regulator to maintain smaller ventilation flow. Since there was limited particle separation reported, and due to the time limitation of the experimental testing the cyclone separation of the spray frozen particles was not terminated but postponed for future testing. In the mean time the frozen particles were collected from the spray freezing chamber in a cooling box, and transferred manually into the fluidization vessel.

# 3.3.5.4.3 Spray freezing chamber

No problems were noticed during the spray freezing operation, there was good freezing gas flow out the chamber, less clouding, and a steady temperature control near the spraying point and the outlet as well as wall temperature. But the major problem encountered was the particle adhesion to the walls due to roughness, that required the occasional tapping on the conical section of the chamber.

# 3.4 Cryo-spray freezing-drying

In this experiment liquid concentrate is sprayed directly into liquid nitrogen for rapid freezing is commonly preformed in lyophilisation of microbiological samples (Sonner 2002). The speed of freezing influences the rate of ice crystal nucleation. Fast freezing rate produces small ice crystals and possibly cause a higher resistance to sublimation mass transfer. The operational plan is to spray a concentrated liquid material into a cryogenic medium and then freeze-dried this in under low pressure in a conventional freeze-drier. This experiment aim is to investigate the effect of two different freezing rate processes on the freeze dried particulate. The primary interest is the influence of the freezing rate on the structure of the product followed by other comparative analysis such as denaturation, volatile retention and particle sizing and dryness.

The experimental setup had some technical problems mainly relating to the spray freezing operation. The first concern was the vaporisation of the cryogenic medium that results in the spray first contacting cold gas and possibly freezing before contact is made with the liquid. In addition the risk of nozzle blockage here is higher than the spray freezing chamber as the operational temperature is lower. The sprayed liquid freezes when released from the nozzle and may form a crust or lumps on the surface of the cryogenic medium.

# 3.4.1 Spraying nozzles and operation set up

The spray nozzles used in this experimental rig were the same used in the spray freeze-drying rig, with the same setup conditions and feeds operations with the exception that it was preformed outside the of the spray chamber. These were

- XA Pr050 pneumatic nozzle operating at 3 bar atomisation gas pressure and 2 bar liquid feed pressure, and the
- WL 0.253 hydraulic nozzle operating at 5.5 bar liquid feed pressure.

The point of spray release was set to 6 cm above the liquid feed to allow sufficient spray disintegration and the spraying period is allowed to a significant time of maximum evaporation of 1 cm deep for f the freezing liquid. The spray nozzles were protected from

freezing and blockage using hot air fed inside the nozzle holding cylinder in addition to thermal heating of the nozzle body (maximum level), as applied in the previous chamber setup.

#### 3.4.2 Spray freezing chamber

The proposed design was similar to that operated by (Sonner 2002), see figure (3-27). The freezing medium was placed in a stainless steel vessel to the correct height and the vessel was then placed on magnetic stirrer for agitating the freezing medium pool and preventing a crust forming on the frozen spray powder produced. The vessel was closed in order to reduce external contamination, though having venting outlet to prevent pressure build up inside the vessel. The freezing medium used here was liquid nitrogen LN<sub>2</sub>. During the spray freezing the temperature of the gaseous headspace was recorded in the range of (-185  $\pm$  -5 °C).





# 3.4.3 Product freeze-drying

The spray-frozen particle transferred in a slurry form of particle- $LN_2$  into pre cooled freezedrier flask. These flasks were then placed in polystyrene cooler containing a metal block cooled with liquid nitrogen to cryogenic temperature at the base to keep the flasks cooled until they were attached to the freeze-drier.

The drying time is not easily assessed therefore all samples are dried to a duration of at least 24 hours, to assure all the materials were dried. The freeze-drier used for this experiment was BOC Edward Modulyo Freeze-drier with operating capacity of  $-50^{\circ}$ C of condenser, and the latent heat of sublimation provided by the surrounding air. The samples are dried at pressures as low as 6.4 mbar and ambient chamber temperature. The freeze-drier was switched on and allowed to reach the set condenser temperature and operating pressure by the time the sample was attached.

The pump attached to this freeze-drier was a  $5m^3/hr$  BOC Edward vacuum pump. Complications where caused by the flasks being filled with cryogenic slurry of liquid nitrogen and frozen particles, as the presence of a small portion of  $LN_2$  in flask evaporates to many hundreds times its volume and this may exhaust the pump capacity. The resulting pressure build up had resulted in a rise in sample temperature due to lack of sublimation and cause sample collapse and failure of the freeze drying operation

The alternative arrangement was made is to freeze dry the sample inside the vacuum fluidisation vessel using the power of the vacuum pump as mass remover of nitrogen gas and the heat of sublimation is provided by the ambient heating, if required heated nitrogen gas applied. In this approach the real difference between the spray freeze-drying (SFD) and cryospray freeze-drying (Cryo-SFD) is the freezing rate. Here the sample were placed inside the QVF vessel closed from one end and placed inside the vacuum vessel while the spring disc is removed.



Figure 3-28: The spray freezing rig.



Figure 3- 29: The Modulo freeze-drier

Summary in this chapter the three experimental rigs design, construction and operation of the three experiment rigs has been described. The testing of the production performance of these rigs was based on the assessment of the product quality and measurement results of the spraying characteristics seen in the next chapters.

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# Chapter 4

# Materials and Methods of Characterisation

#### 4.1 Introduction

This chapter describes the materials used in the study and the methods of characterising them both pre processing when they are in a dissolved liquid state and post processing when they have been dried into a particulate.

The liquid characterisation involved measurements of parameters, which would be likely to affect how the material is processed. For example, surface tension and viscosity have known to affect atomisation of liquids. Refractive index was measured to determine the extent of refraction of the laser beams by liquid droplets during the PDA characterisation of the spray. The DSC was carried out to understand the phase behaviour of the studied solutions (i.e. melting and glassy transition temperatures).

Solid characterisation measurements were performed to assess the affect of the processing conditions on the physical properties of the resulting product, such as bulk density, particle density, moisture content, particle size distribution and surface area and porosity. For each material a functional properties were also identified which would reflect the quality of the product. The properties chosen were the extent of protein denaturation for the whey formulation, retention of aroma components for the instant coffee, finally the drying processing of sticky (sugar rich) materials such as sucrose solution.

The results for the characterisation of solid particles from different methods are presented in chapter 6 specific sections related to the process concerned. The results for the liquid characterisation tests are more generally relevant and apply to all experimental and drying processes. These results are therefore included as part of this chapter.

# 4.2 Processed materials used for spray drying/freeze-drying

# 4.2.1.1 Whey protein isolate (WPI) powder

Whey proteins are a constituent of milk. Whey protein solutions are a bi product of cheese making process, and contain mineral and lactose as well as proteins. An ion exchange adsorption separation process can be used to reduce the mineral and lactose content of the solution. The proteins are initially adsorbed on to the ion exchange, and then eluted by raising the PH to a value higher than 5.5 where it is then ultra filtrated and thereafter dried. The resulting product is termed whey protein isolate powder, which contains more than 85% protein.

Whey protein isolate powder (ex Ultimate Nutrition Fleetwood, Lancashire,UK) was used in this study. The product specification is virtually lactose free, 23% of the protein present are branched amino acid chains, and it is claimed that more than 99% of the whey proteins are un-denatured. The whey powder is completely soluble and instantised for easy mixing in water.

# 4.2.1.2 Compositional information

The following general compositional information supplied by the manufacturer.

	(Dry Basis per 100g)
Protein	92.0g
Carbohydrate	3.0g
Of which sugars	3.0g
Fat	1.0g
Fibre	Nil
Sodium	200mg
Calcium Content	400mg
Lecithin (E322)	

# 4.2.1.3 Whey protein concentrate preparation

The preparation of the concentrate was based on a mass of 1 kg of concentrate 30% (w/w), starting from weighing 300 g of whey protein isolate (WPI) and 700 g of distilled water separately. The protein powder was difficult to disperse and dissolve in water, and required mechanical agitation. This was achieved using the "Silverson" heavy-duty laboratory mixer.

The powder was added to water in a deep 2 litres volume beaker, with a stirrer blade rotating at the minimum speed setting and at 1-2 cm below the water surface. Powder was added in three batches, to avoid splashing and spattering of the powder, and leaving the mix to blend well for 2 minutes after each addition. This method was found to be much faster than using a magnetic stirrer. The produced concentrated mix has some insoluble residues that are precipitated by centrifugation. Thence the mix is filled into 4 centrifugation bottles, however this concentrate foam during mixing (foaming is one characteristic properties of the whey protein), the mix should be loaded into the centrifuging bottles as quickly as possible to have even weight distribution between the bottles before collapsing and separation of the foam. The centrifuge bottles are 500 ml polycarbonate containers filled and placed into "Beckman J2-21M/E centrifuge with a JA-10 rotor". There is no agreement between the researchers on the time and the speed of the centrifugation, as each has own specific method and application of analysis, so the decision is left to the researcher need and judgment. For this research separation of the soluble concentrate from the precipitate is adequately achieved at 2000 rpm speed for duration of 20 minutes. Before atomisation operations the separated soluble concentrate were filtered from any lumps through 0.5 mm mesh.

# 4.2.2 Soluble coffee

Soluble coffee is the extract product of roast coffee beans arising from a high temperature series of water-based extractions. Coffee beans typically contain 25-30% soluble solids <sup>(10)</sup>. After the extraction stage the solution is concentrated by evaporation to 30-40% before being either spray dried or freeze dried to produce an instant soluble coffee powder or granules <sup>(5, 10)</sup>. There are more than 400 characteristic components in coffee beans including soluble solids, insoluble solids, oils and volatiles.

Most of the volatile compounds present in the coffee extracts are vaporised and lost during drying, hence instant coffee manufacturer often trap these compounds (specifically the spray dried coffee) and add them to the product prior to packaging. The presences of these volatiles compounds are key to the perceived quality of a coffee drink by a consumer. The most commonly occurring volatiles are listed in table 4-1.

The volatile constitute a level of approximately 1.1 % (w/w) prior to drying. The aim of the volatile analysis in this research is to quantify the ability of different spray and or freeze drying processes on the retain volatiles in the end products. Acetone, which typically account

for 18% (w/w) of the volatile compounds was chosen as marker compound. Acetone is a ketone, which has molecular weight of 58 kg/kmol and a boiling point of 56 °C. its the relative vapour pressure (volatile/water) is 60 at 100 °C. It is of a medium importance to the flavour of coffee compared to other components (Johonson *et al.* 1974, Desrosier *et al.* 1979).

	Mol (Wt)	%	Boiling Point (°C)	Relative Flavour Importance*
Acetaldehyde	44	19.9	21	1
Acetone	58	18.7	56	2
Diacetyl	86	7.5	88	1
<i>n</i> -Valeraldehyde	86	7.3	102	2
2-Methylbutyraldehyde	86	6.8	91	2
3- Methylbutyraldehyde	86	5.0	91	2
Methyl furan	82	4.7	63	2
Propinoaldehyde	58	4.5	49	2
Methyl formate	60	4.0	32	2
Carbon dioxide	44	3.8	-78	-
Furan	68	3.2	32	1
Isobutyraldehyde	72	3.0	63	1
Pentadiene (isoprene)	68	3.0	30	2
Methyl ethyl ketone	72	2.3	80	2
$C_4$ - $C_7$ paraffins and olefins	-	2.0	35	2
Methyl acetate	74	1.7	57	2
Dimethyl sulphide	62	1.0	38	1
<i>n</i> -Butyraldehyde	72	0.7	75	1
Ethyl formate	74	0.3	54	2
Carbon disulphide	76	0.2	46	2
Methyl alcohol	32	0.2	65	3
Methyl mercaptan	48	0.1	6	1

 Table 4-1: Some volatile compounds in coffee, table extracted from Encyclopaedia of Food Technology and Food Science Vol. 2. (Johonson et al. 1974).

\*1 = large, 2 = medium, and 3 = small.

Some researchers investigated the field of volatile retention have used the a mixture of acetate (ethyl, propyl, butyl, and pentyl acetate) (King 1979), King et al (1982) had used ethyl and pentyl acetates as markers to measure the volatile loss by atomisation during spray drying. However, others like Mumford et al (1999) had used the acetone in conjunction with ethanol and methanol as a marker inoculate in the volatile retention study. Though the acetone addition into the coffee concentrate may dissolve the volatile retaining surfactant present in the soluble coffee concentrate (Frey *et al.* 1986), but due to the simplicity of acetone handling and that it is the second highest component present in coffee aroma it has been selected as an

added marker for the volatile retention investigation. In this study the acetone precursor use restricted to qualitative determination of overall acetone loss as evidence of reconstituted products collected from different spraying and drying processes, leading the conclusion to aromatic volatile retention analysis.

The coffee material used in this research was "Soluble coffee is an instant J. Sainsbury own brand agglomerated spray dried coffee". Two different concentrates are been used in the comparative study of the drying process investigated in this research, pure soluble coffee concentrate and soluble coffee concentrate inoculated with acetone (volatile precursor).

# 4.2.2.1 Coffee concentrate preparation

The concentrate is prepared by dissolving 300 gram of soluble coffee from a sealed container in 700 gram of distilled water (ambient temperature). The mix is stirred gently on magnetic stirrer for 5 minutes till a complete concentrate consistency, then the concentrate is covered an prepared for spray drying and or freeze-drying. The concentrate inoculated with the volatile precursor is prepared in a similar procedure and quantities; the difference is the addition of 3.3 grams of analytical grade acetone (0.33 % w/w). The addition of the acetone is delayed till the last moment of drying process to minimise the loss of volatiles. A sample of the pre and post inoculation is collected and cooled rapidly in a freezer for the volatile content determination.

#### 4.2.3 Sucrose sugar

The sucrose used was a commercial granulated Tate and Lyle sugar brand purchased from local stores. The concentrate was prepared by dissolving 300 grams of the sugar granules in 700 grams of distilled water at ambient temperature the mix is stirred for 5-10 minutes on a magnetic stirrer until complete dissolution of the sugar granules was visually observed.

# 4.3 Methods of characterising liquid materials

# 4.3.1 Viscosity

The viscosity measurements were carried out using a PC driven HAAKE, VT550 Conette Viscometer with NV sensor at ambient temperature (21 °C). The accompanying HAAKE Software automatically calculates the viscosity values. Each liquid sample prepared was tested three times. Thee average reading of each test run was obtained and the three readings averaged to give an overall viscosity value.

# 4.3.2 Surface tension

The surface tension of processed liquid materials was measured using a counter leaver balance (White Electric Instrument Co. Ltd). Here a platinum ring of known area is hooked on to a balance leaver and immersed just below the surface of the small liquid sample. The sample dish is lowered away from the hanging ring and the surface tension of the liquid exerts a pulling force on the lever, until the platinum ring break away from the sample surface. The maximum force is then recorded. The measurement is repeated 4 times and the average surface tension value of the concentrate is obtained. All tests were carried out at an ambient temperature of 21 °C.

# 4.3.3 Density

Liquid density was measured gravimetrically by a weighing a mass of a sample in a known volume of a pycnometer flask. The density is simply the ratio of the mass to its volume.

# 4.3.4 Refractive index

Refractive index measurements were required for solutions used in Phase Doppler Anemometry (PDA) experiments to enable quantitative size information to be obtained. The refractive index was therefore measured with Billingham refractometer.

A few drops of the sample liquid are placed on the transparent plate illuminated with a halogen lamp. The angle of the refracted light beam is read off a magnified scale from the view port of the refractometer.

# 4.3.5 Differential Scanning Calorimetery (DSC)

The success of freeze-drying processing is largely dependent on creating and maintaining a solid porous structure of the frozen material. Understanding this is key to formulating, planning and operating the process efficiently. This requires prediction of the thermal (phase) behaviour of the material (Roos *et al.* 1991, Blanshard *et al.* 1993, Oetjen 1999).

Biological materials can contain both crystalline and amorphous regions. The crystalline regions are subject to melting whereby the solid structure is lost as the material temperature exceeds the melting point. The amorphous regions can undergo a glass transition whereby the material changes from hard and glassy to a highly viscous (solid) and rubbery over a relatively narrow temperature range. In freeze-drying operations "collapse temperature  $(T_c)$ " is often defined which is the temperature above which the material must not be raised in order to preserve the solid structure. The melting temperature of the crystalline region or the glass transition temperature of any amorphous region determines the collapse temperature.

The temperature range above  $T_g$  and below  $T_m$  presents the material in the rubbery amorphous form this allows better degree of molecular motion thence better possibility of crystallisation or sublimation (Lozano 2000), however the collapse risk is higher. Thermal characterization of the freeze-dried substances is important for a rational operation, so the freezing and primary drying processes can be progressed in a rational basis, it would indicate in a proximity values of thermal properties that is required for processing, such as glass temperature ( $T_g$ ) and melting temperature ( $T_m$ ).

DSC usually used to detect the change in the morphological structure due to heat flow through the sample, described in a phase change curve (Mellor 1978, Jennings 1999, Oetjen 1999). The spray freezing in the SFD process encountered in this research has a degree of rapidity, not as cryogenic freezing that is to be confirmed from the degree of crystallisation measurement. The polymeric materials thermal transition characterisation usually preformed by the Differential Scanning Calorimeter (DSC). It is an analytical method measures the heat flow of freezing and melting through a matter held under isothermal conditions, depending on the rate of cooling and heating, which are influenced by the content of the matter. The differential scanning calorimeter is capable of obtaining thermal profile, to a certain degree of accuracy can be used to identify the glass state temperature and the predict the onset range of melting temperature, which are needed in freeze drying operations to decide and select the operation condition of a specific material formulation.

# 4.3.5.1 DSC-Principles of operation

In this method of analysis the difference in heat flux (power) between the sample and a reference cells is measured as a function of temperature and or time while subjecting the cells to a controlled temperature programme. The heat power supplied per unit time  $\left(\frac{dQ}{dt}\right)$  described as

Where Q is expressed in joule (J) or joule per unit mass (kJ.kg<sup>-1</sup>).

The instrument used in this research study is a power compensated Differential Scanning Calorimetry (DSC). The principle of this thermal analysis, the sample in sealed aluminium pan and an empty reference pan placed in separate self-contained calorimeters with own heater elements and thermocouples (see figure 4-1). The heating for both calorimeters controlled separately so that the pans follow the same temperature-time profile. The temperature difference between the sample and reference cells calorimeters is maintained to zero, it the instrument fundamentally measures the energy flow in a sample. In a constant rate of heating the calorimeter compensate for the energy change occurring in the sample by heating power supply, and the difference in power of the two pans is directly related to the enthalpy change of the sample. The output of a DSC measurement of the phase-change (melting endotherm) will manifest as a peak over and above the specific heat "baseline", and the area under the power vs time plot is the enthalpy of the phase change.



Figure 4-1: Schematic diagram of DSC.

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The enthalpy change is the quantity of heat absorbed or released  $\Delta H$  (kJ.kg<sup>-1</sup>) expressed by

$$\Delta H = \int_{T_1}^{T_2} \frac{dH}{dT} dT \qquad \text{Eq (4-2)}$$

Where H is the enthalpy detected by DSC and  $T_{1\&2}$  are the temperature range measured.

$$\Delta P = Q = \frac{dH}{dt} = m\frac{dh}{dt}$$
 Eq (4-3)

Where m is the mass of the sample (kg), and dh is the enthalpy change at a temperature change interval. If no phase-change occurs

$$dh = C_p dT Eq (4-4)$$

Then

$$\Delta P = mC_p \frac{dT}{dt} = mC_p \alpha$$
 Eq (4-5)

Where  $\alpha$  is the rate of temperature change per unit time  $\left(\frac{dT}{dt}\right)$ , and  $C_p$  is the specific heat capacity at constant pressure (J.kg<sup>-1</sup>.°C<sup>-1</sup>).

The series of equations (4-1 to 4-5) explain the capacity of DSC in determining some of the material thermal properties from the heat flux, such as conversion to  $C_P$  by dividing the enthalpy change of the mass temperature-scanning rate.

The DSC thermograms are presented as power per unit sample mass by dividing the DSC power signal by the measured sample mass in each case, enabling better comparison between samples.

#### 4.3.5.2 Data Interpretation

The DSC thermogram in general shows two types of thermal event of phase transition during warming, from these the  $T_g$  and  $T_m$  can be predicted. Firstly a glass transition can be detected from a slight change in the sample heat capacity (or in the DSC power). The  $T_g$  identified in this inflection by three points onset, mid and end points glass transition temperatures  $(T_g^i, T_g^m, and T_g^e)$ . They are characterised by drawing two lines parallel to the

Both  $T_g$  and  $T_m$  can be subjected to error as different heating rate can lead to different temperatures. Also the prediction construction used are sensitive to minor changes in the shapes of the DSC curves, the  $T_g$  in particular is sensitive to the operator interpretation as the specific heat capacity associated with  $T_g$  is often small and easy to over look or misinterpreted.

# 4.3.5.3 Experimental procedure

All three liquid substances (coffee, whey protein, and sugar) were analysed by DSC in different concentrations (10, 30, and 60 % solute content) in order to obtain a understanding of the substance phase transition, even though the concentrates substance used for freeze-drying contained 30% solute content.

One or two drop of these concentrates placed in a pre-weighed pan and the net weight of sample was recorded, the pan is the sealed, and rechecked in weight. Two cells are made the first one is empty and the second filled with the liquid sample.

These cells are placed in the thermal analysis chamber of the DSC and cooled rapidly at Cooling rate 80 °C per minutes down to -55 °C. The rate of cooling applied in this analysis was relatively close to that of the spray freezing (in gaseous) process, in order to obtain a representative heat flux transition through the analysed materials. Then the sample re warmed 1.5 °C per minute rate. The DSC instrument used in this analysis was a Perkin Elmer (Pyris Dimond DSC), at Nottingham University-Division of Food science.

# 4.3.6 Results of the liquid materials Characterisation experiments

The measured physical properties of the processed liquid material are listed in table 4-2. The glass transition and melting temperatures produced from the DSC experiments are listed in tables 4.2 - 4.4. The thermograms used in obtaining these results are shown in figures 4-4 to 4-6.

	Surface tension (dyn/cm)	Viscosity (Pas)	Density (kg/m³)	Refractive index
Distilled water	72.9	0.00108	972.8	1.33
30% sugar solution	56.4	0.00396	1087.6	1.38
50% sugar solution	58.4			1.42
30% Coffee solution	44.3	0.00830	1120.6	1.39
30% soluble coffee + acetone 0.33 %	41.1	0.00918	1102.9	
30% Whey Protein Conc.	46.1	0.02720	1044.9	

# **Table 4-2:** Measured physical properties of the spray-dried solutions.

 Table 4-3: Glass transition and melting temperatures of 10, 30, and 60% whey protein concentrates as measured by Differential Scanning Calorimetry.

	Glass transition temperature $T_g$ (°C)			Melting temperature $T_m$ (°C)		
	T <sub>go</sub>	T <sub>gm</sub>	T <sub>gf</sub>	T <sub>mo</sub>	T <sub>mp</sub>	T <sub>me</sub>
Whey protein conc. (10%)	****	****	****	-0.2	1.9	3.5
Whey protein conc. (30%)	****	****	****	-1.3	0.7	1.4
Whey protein conc. (60 %)	****	****	****	-13.4	-5.9	-4.1

 Table 4-4: Glass transition and melting temperatures of 10, 30, and 60% soluble coffee concentrates as measured by Differential Scanning Calorimetry.

	Glass transition temperature $T_g$ (°C)			Melting temperature T <sub>m</sub> (°C)		
	T <sub>go</sub>	Tgm	T <sub>gf</sub>	T <sub>mo</sub>	T <sub>mp</sub>	T <sub>me</sub>
Coffee conc. (10%)	-27.0	-25.8	-24.5	-2.3	1.3	2.6
Coffee conc. (30%)	-26.1	-24.9	-23.7	-5.1	-0.6	0.6
Coffee conc. (60 %)	-34.6		-23.7	-21.6	-5.4	-4.8

Table 4-5: Glass transition and melting temperatures of 10, 30, and 60% sucroseconcentrates as measured by Differential Scanning Calorimetry.

	Glass trans	Glass transition temperature $T_g$ (°C)			Melting temperature T <sub>m</sub> (°C)		
	T <sub>go</sub>	T <sub>gm</sub>	T <sub>gf</sub>	T <sub>mo</sub>	T <sub>mp</sub>	T <sub>me</sub>	
Sucrose conc. (10%)	-35.8	-34.4	-32.9	-2.3	1.4	2.7	
Sucrose conc. (30%)	-35.2	-33.7	-32.3	-7.1	-0.8	0.2	
Sucrose conc. (60%)	-36.8	-35.4	-34.1	-25.9	-6.7	-5.9	



Figure 4-4: DSC thermograms of whey protein concentrates.



Figure 4-5: DSC thermograms of soluble coffee concentrates.



Figure 4-6: DSC thermograms of sucrose concentrates.

The glass transition temperatures of sucrose concentrate were clearly detectable and in the range of -33 to -36 °C. This result is not far from Slade and Levine (1991) results -32 °C  $T_g$  for a maximally freeze-concentrated sucrose system <sup>(232)</sup>. The Tg transition temperature for coffee concentrates had been also easily detectable, however a broader distribution of 2-10 °C was noticed depending on the solute content of the concentrate.

The glass transition temperature  $(T_{gm})$  of whey protein concentrates was not detectable from the thermograms obtained of the analysed samples and thus values were not reported. Roos  $2000^{(232)}$  reported that due to the broadness of the transition changes and the small changes in the heat capacities it is often difficult to determine the glass transition temperature of proteins. As the  $T_g$  value indicated in the above tables (4-3 and 4.4) for coffee and sucrose concentrates are 20 to 30 °C below the onset of melting temperature, it is possible that the  $T_g$  value of the whey protein concentrate also in this range. However it will be necessary to perform freezedrying at a range of temperatures in order to ascertain value for the freeze-drying collapse temperature  $(T_c)$ .

In a typical Calorimetric analysis a sequence of sample repeat and standard of sampling technique is followed in order to obtain a relatively confirmed reading of a material transition properties. In this research one analytical test carried for each sample subjects the results to scrutiny of doubt. Since the aim of this analysis is to obtain a guideline  $T_g$  and  $T_{mo}$  values for freeze-drying certain materials, these results would be used with a marginal caution of 2-5 °C to avoid product melting or collapse.

For the spray freeze-drying process a 30% concentrates were processed, so their  $T_g$  and  $T_{mo}$  were more important to select a safe freeze-drying operation temperature range avoid the collapse or melting the particulate. These values are 2 °C below the  $T_{go}$  and maximum up to  $T_{gm}$ , for

- Coffee concentrate -27± 2 °C,
- Sucrose concentrate is  $-36 \pm 2$  °C, and
- For whey protein concentrate it will be tested stating from -25 ± 2°C for operation with no collapse and optimum drying rate.

A striking feature of these experiments is that with the 60% coffee concentrate there is a distinct lack of variation in the glass transition temperature with initial sample moisture

content. This can be attributed to the theory that the glass transition is occurring each time in the maximally freeze concentrated portion of the sample, the moisture content of which is invariant. The difference between the samples of different initial moisture content can be assumed to lie in the different proportion of the sample that will freeze as a pure ice. This can be verified by examining the enthalpies of melting peaks (per unit mass of a sample). They are much larger for the samples with higher initial moisture content. Table (4-4 and 4-5) the melting peak areas for each sample and the mass fraction that has crystallised as pure ice assuming the latent heat of melting of water 333.5 kJ.kg<sup>-1</sup>.

In table (4-4), the  $T_{go}$  of 60% coffee concentrate reported an irregular reading of -34.5 °C that is not close range with other concentration of the same sample, this may attributed to either sample contamination, or the melting peak extension leading to a merger or interference of the glass transition end with the onset of melting, which means reducing the temperature range between glass transition state and the concentrate melting. The general practice of DSC characterisation is to have repetition of the sample analysis for consistency check, unfortunately in this research only one test sample was analysed.

# 4.4 Methods of characterising particulate materials

The produced particulate varies in the degree of the physical absolute and bulk properties, results from the effect of processing conditions on the certain functional properties of the particulates. In this section the physical and functional properties of are defined and the methods of measurements described. Some physical properties were measured for all samples obtained, these are moisture content, absolute and bulk density, particle size distribution, the particle surface area and porosity, and finally particle morphology. Other parameters which were characteristic to individual processed materials determining the effect of processing on the functional properties such as the volatile retention, whey protein denaturation due to thermal degradation. These properties are selected for a comparative study of the process performance on particulate produced by spray drying, rapid spray freezing with conventional freeze-drying and finally the spray freeze-drying processes. The analysis method procedure and description of these properties of particulate are described in this section.

# 4.4.1 Bulk density

Bulk density is the ratio of the particulate sample mass, including the moisture content, to the volume it occupies. There are three different types of bulk density measurements which is depends on the sample preparation, which affect how the sample packs in the measured volume space.

- As-poured, bulk density obtained from a sample heaped in the container without any compacting forces.
- Compacted, the bulk density of sample added to the container with the aid of compaction forces.
- "Aerated" bulk density, applied only to dry and fine powders when the particle separated from each other by air film (BMHB 1983).

Compact bulk density is the characteristic property of the of dried particulate is chosen in this research as the particles produced are transferred number of times before measuring the bulk density, also the produced particles are so hygroscopic and cohesive and therefore it was not easy to obtain a clear reading line of the volume in the measuring container. The sample poured in the cylinder and tapped 3-5 times gently till a clear reading line is obtained.

This value is determined by pouring a mass of a sample in an empty and dry measuring cylinder with a known weight when empty. The total weight is then measured for this cylinder. The level of the volume is then read and recorded. The Bulk density is then determined from the following equation

Bulk Density 
$$(\rho_{\rm B}) = \frac{Mass \, s \, of \, ample}{Volume \, occupide \, by \, sample}$$
 Eq (4-6)

#### 4.4.2 Absolute density

Particle density is the ratio of the solid matter mass to the volume of the solid excluding voids. It can be measured using a gas displacement technique. A known mass of particles  $(M_{sample})$  is loaded into a sample sell of known volume  $(V_{cell})$ , which is then charged to a pressure  $(P_1)$  with inert gas. The sample is connected via a valve to a second chamber with a volume  $(V_{exp})$ , which is initially evacuated. On opening the valve the chamber pressures equalise, and the final pressure  $(P_2)$  enables the volume of the particles to be calculated using the equations (4-7 and 4-8).



Figure 4-7: A schematic sketch of the chamber for solid matter density measurement

$$V_{sample} = V_{cell} - \frac{V_{exp}}{\frac{P_1}{P_2} - 1}$$
 Eq (4-7)

Five pressure filling and venting readings are taken and the results of the volume are averaged. Knowing the initial mass of the sample allows the determination the particle absolute density  $\rho$  from equation (4-7).

$$\rho = \frac{M_{sample}}{V_{sample}}$$
 Eq (4-8)

The measurements of is carried out using Micromeritics Multi-volume Pycnometer 1305. The used cell has a volume of  $(V_{cell})$  7.772262 cm<sup>3</sup>, and the expansion volume  $(V_{exp})$  6.15619 cm<sup>3</sup>.

#### 4.4.3 Moisture content

The moisture content of the particulate samples was measured gravimetrically. Aknown mass of sample was placed in an aluminium dish and dried in a vacuum oven at  $105 \pm 5$  °C for a period of up to 24 hours an weighed at regular intervals. The weighing proceeds as follows samples are removed from the oven, placed in desiccator and allowed to cool for 1-2 minutes before being weighed as quick as possible. The total duration is not exceeding 5 minutes. The samples were weighed on the hourly basis for the first 8 hours to assess the drying rate. A final weighing was preformed after total drying time of 24 hours, after which the sample assumed is bone dry. The final weight is then used in the calculation of the moisture content based on equation (4-9). Two replicate of each samples were measured and the average moisture content is obtained.

$$%moisture\ Content = \left(\frac{Initial\ Sample\ Mass - Final\ Sample\ Mass}{Dried\ Sample\ Mass}\right) \times 100 \qquad Eq\ (4-9)$$

For sucrose sample the above drying temperature was found to be too high and this could lead to caramelisation of the particles. Therefore the oven temperature was set to  $55 \pm 5$  °C, which was chosen to be below the glass transition temperature of sucrose (63 °C).

# 4.4.4 Particle sizing

The dried product particle size was characterised using Coulter LS 130 laser sizer. The principle of operation of this instrument is by detecting the reflection of scattered light caused by the passage of a particle through a laser beam. This instruments measures particle sizes in the range  $0.4-900 \mu m$ .





A suspension of dispersed particles is placed in a housing cell, which is sealed with a circular side glass. The particles are stirred within this cell and their motion interrupts the path of a laser beam. The particle size affects by diffraction pattern, of light through a Fourier lens that is focused on the photo detector as indicated in figure (4-9). The lens is only sensitive to the angle of incidence of the laser beam and not to the position of the source light.

The LS130 particle sizer used "Polarisation Intensity Differential Scattering" (PIDS) light method. It uses an incandescent tungsten-halogen lamp and three sets of vertically and horizontal polarized filters to provide a monochromatic light at different waves length. This light is focused in a slight divergent through a spatial filter (slit) and projected on the PIDS sample cell. The light is decomposed into vertical and horizontals polarized components, which refers to the direction of oscillation of the light's electric field. The small angle of diffraction of light from the particle surface specifically for the large particles according to Fraunhaofer diffraction is more sensitive to polarisation.



Figure 4-9: Schematic diagram of the particle measurements in Coulter LS130, Fourier lens focusing.

The intensity of the light scattered perpendicularly to the flow is measured by the five photo detectors in the PIDS assembly, while the sixth detector measures the un-scattered light intensity to quantify the obstruction resulted from the particle presence in the sample cell, interrupted the light path. The resulting signals are transferred to a PC where accompanying software produces a statistical data of the obstructions detected in the sample cell. The results are presented in the form number fraction of particles with wet size range bins and also mean, median, and standard deviations particle size.

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Figure 4-10: Components of Coulter LS130 (Picture taken from Coulter Reference Manual 4235896-C).

Using "Coulter LS130 Laser Sizer requires suspending the particles in a non solving medium or dispersing fluid. The suspension fluid should be a transparent, non-viscous, non-dissolving of the sample particles, consistent, and have a density lighter than that of the sample particles. The most commonly used dispersion liquid for sugar, milk and milk products are (Bornhardt 1994)

- Iso-butanol
- Iso-butanol + Dethylphtalate
- Iso-amyl alcohol.

The non-solvent liquid for coffee powder is mineral oils. For the purpose of selecting a common dispersing liquid for all samples, isobutyl alcohol was tested for coffee powder solubility. The results showed that coffee is also insoluble in isobutyl alcohol; therefore it was chosen to be the dispersing liquid for all samples produced in this research.

Each batch of dried particulates was tested in triplicate. The results of particle distribution obtained from the Coulter Laser sizer data for these samples are plotted in terms of fractional percentage distribution of size range in relation to the total particle number present in the sample. The particle size range is expressed as the 95% confidence interval of the cumulative distribution of the total particles analysed from each batch (Holdich 2002), the particles size consisting the populations between 2.5% and 97.5% of the total cumulative distribution of the particle batch.

# 4.4.5 Surface area and particle porosimetry

The principle in this measurement is the adsorption of gases and vapours on to the surface area of finely divided or porous materials. The adsorption isotherm obtained also to produces significant information about the energetic heterogeneity and geometric topology of the sample under study. The adsorption isotherm can be modelled using simple theories for adsorption such as mono-layer Langmuir and BET equations. These can be used to give an approximate estimate of the surface area.

Nitrogen gas from a liquid nitrogen dewer is physically adsorbed by the test sample and the amount of nitrogen adsorbed at various pressures is determined either volumetrically or gravimetrically. These data are plotted according to BET-equation parameters. From the slope and intercept of the linear BET-plot the mono-layer capacity is determined. Using Avogadro's number and the area occupied by a molecule of nitrogen while adsorbed on the surface under investigation, the surface area of the material can be calculated.

The porous nature of the sample is characterized by distribution of pore sizes assuming each pore acts independently. The size of each pore size present then contributes to the total adsorption isotherm in proportion to the fraction of the total area of the sample that it represents. Mathematically, this relation is expressed by

$$Q(p) = \int f dH \cdot q(p, H) \cdot f(H)$$
 Eq (4-10)

Where

Q(p)

= the experimental quantity adsorbed at pressure p,

q(p,H) = the quantity adsorbed per unit area at the same pressure, p, in an ideal pore of size H, and

f(H) = the total area of pores of size H in the sample.



Figure 4-11: The ASAP 2010 Chemi System (Picture taken from Macromiteric Catalogue).

The equipment used for this characterisation was "ASAP 2010 Chemi System", a volumetric adsorption apparatus, from Macromiteric (USA). The analysis carried out in the Chemical Engineering Department at Loughborough University, by Dr. D. J. Malik.

The technique is widely used in the characterization of fine powders like freeze dried and spray dried adsorbents like alumina, silica, activated carbon granules and fibres, cloth, felt, and molecular sieves. In this research the method is used to characterise foods particulate produced by the spray drying and spray freeze-drying.

#### 4.4.6 Gas chromatography

Gas chromatography (GC) is most the widely used method for the qualitative and quantitative analysis of volatile components in sample mixtures. Typical applications include detection traces of hydrocarbons and the pollutants in air or water, the detection of pesticides, aromas and flavours in the food industries. In pharmaceutical and medicinal science it is used to test for the presence of drugs in blood, breath and other bodily fluids.

GC is a volatile separation technique, achieved by repeated distribution of each sample components between two phases. The mixture sample passes (in vapour form) in a gaseous mobile phase (carrier inert gas) through a porous stationary phase contained in a long tube, or column, which separates (or partitions) as it travels along the column due to different affinity of the species to the stationary phase. The basic GC system consists of a carrier gas, a heated sample injection port, a separating column, and a detector, and often is driven by a dedicated computer for data collection, storage, and processing. A GC flow schematic is shown in figure (4-12).

The samples to be analysed can be solids, liquids, or gases. Solid and liquid samples must first be vaporised; thus, they must be heated as they are introduced into the injection port. Normally, a very small volume of sample (on the order of 0.1  $\mu$ L to 50  $\mu$ L) is used. The vaporised sample is swept onto the column by the flow of carrier gas.

The stationary phase most frequently used consists of an inert solid support coated with a nonvolatile liquid. The affinity of the components dictates the type of the stationary material used. The rate of the carrier gas flow through the column is selected to suit good partitioning of the detected peaks as they move through the column at different rates and thus are separated. In general the higher boiling components and those, which have affinity to the stationary phase will take longer to pass through the column. This selectivity of the stationary phase is determined by the functional groups and polarity of the stationary phase substance. The column is placed in temperature-controlled oven, and temperatures varied accurately to suite the separation requirement of the mixture. The detector used then detects these separated components, by either thermal conductivity or flame ionisation methods. The detector used ins research GC analysis is thermal conductive type.



Figure 4-12: Diagram of the GC setup used in the volatile retention analysis of the dried coffee particulates, (picture taken from "Macherey – Nagel" catalogue).



Figure 4-13: The peak separation of a component in the Chromatogram. (Picture taken from "Macherey – Nagel" catalogue). a = overlapped peaks area, b = resolved peaks area

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The resulting chromatogram consists of base line and number of peaks partitioned based on the retention time difference of components passing through the column. The retention time is used to identify a specific compound. The area of these peaks allows the quantification of the component in the sample passing through the column, which is limited to the time of peak initiation to the end of the peak (back to the base line). The accuracy of mixture analysis is dependent on the quality and degree of peaks separation.

The GC technique used in this research to detect and quantifying the volatile loss from the drying process in a comparative study of the spray drying, rapid spray freeze-drying and spray freeze-drying of soluble coffee concentrate which is optimally inoculated with a known mass of acetone. The main component of interest in this mixtures are thus the solvent phase, water and acetone. Water boils at temperature of 100°C at atmospheric pressure whereas the acetone evaporate at 58°C. Therefore an injection temperature of 110°C was chosen to ensure vaporisation of all the main components.

The Chromatograph used was "PYE Unicam 104 Chromatograph" and the data were processed using a "Philips PU 4810 Computing integrator" processor. The column used for in this analysis "FFAP" (Polyethylene glycol 2-nitroterephthalic acid ester) packed column, selected based on the ("Macherey – Nagel" catalogue) recommendation.

# 4.4.6.1 Gas chromatography operation procedure for acetone inoculate detection

The carrier gas flow was first reduced to 33 ml/min in order to obtain good peak separation. The oven temperature was then set at 110 °C to ensure vaporisation of the sample components. Coffee components may boil at higher temperature than that of water and it is recommended to vaporise the material before entering the packing inside the column, to avoid damaging the wax based FFAP (Polyethylene glycol 2-nitroterephthalic acid ester \*) packing.

- Injecting the sample using the following repeatable technique.
- Fill the syringe with sample and then expel, repeated 8-10 times, to ensure the syringe is not contaminated with previous.
- Fill the syringe and expel back into the sample vial, repeat 8-10 times, for assuring the removal of the air bubble from the sample injected.
- Inject 1  $\mu$ l of sample into the column and wait for 10 seconds before pressing the inject button.
- Gently remove the syringe out of the column.

- Allow the integrator sufficient time to return to base line or in the range of  $1000 \pm 5$ .
- For each sample analysed and the middle three peak area values are averaged for considered reading of the peak area against the concentration of the inoculate.
- Five GC experiments were preformed for each sample.

As the interest in this analysis was in the quantification of the retention of one single component (acetone), therefore the peak of other components (including water) were disregarded unless they affected the readings of the acetone peak.

# 4.4.6.2 Volatile retention in coffee during drying

As described in section 5.2.21, some were inoculated with sample of coffee prepared for drying processing 3300 ppm of added acetone. It is important to establish a measured scale of calibrated acetone concentration in water to determine of the concentration of acetone in the analysed samples. To this end a number of calibration solutions of water and acetone were prepared in the following concentration "5000, 4000, 3500, 3000, 2500, 2000, 1500, 1000, 900, 800, 700, 600, 500, 400 ppm (w/w)". Concentrations below 400 ppm were not used as it was difficult to resolve the peak area accurately.

Viol No	Concentration of	Mass of Acetone	Mass of 1000	Mass of water
viai no.	acetone ppm (w/w)	(g)	ppm (g) solution	(g)
1	1.00E+06	10		
2	5000	0.5		99.5
3	4000	0.4		99.6
4	3000	0.3		99.7
5	2000	0.2		99.8
6	1000	0.1		99.9
7	900		10	1.11
8	800		10	2.5
9	700		10	4.29
10	600		10	6.67
11	500		10	10
12	400		10	15
13	0		0	10

 Table 4-6: Calibration solution preparation.

Two procedures were followed in the preparation of these solutions. Samples with concentration greater than 1000 ppm were prepared by directly adding the required amount of analytical grade acetone in a 100 ml vial and then adding distilled water to make up 100 g. Samples with concentrations less than 1000 ppm were prepared from 1000 ppm solution made

by the previous procedure. A quantity of this solution was then diluted with the required amount of distilled water. A summary of these samples preparation and masses of acetone and water mixed are listed in table 4-6.

# 4.4.6.3 Acetone water calibration

For peak area determination, an average of the middle three values was taken in each case. A calibration plot showing the variation of peak area with acetone concentration is shown in figure (4-15). A linear fit was established which is given in equation (4-11).

$$A = 2.1826 \times C$$
 Eq (4-11)

$$C = \frac{A}{2.1826}$$
 Eq (4-12)

Where

1 3

A C = inoculate peak area,

= concentration of the inoculate corresponding to the peak.



Figure 4-14: Calibration peaks of water inoculated with acetone (A) 3500 ppm, (B) 400 ppm. Peaks are detected by Pye series Gas Chromatograph using FFAP packed column at 110°C.

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Figure 4-15: GC Calibration plot (peak area Vs acetone concentration). The graph shows data prints and the line of best fit ( $R^2$ = 0.998).

# 4.4.7 Protein denaturation

Whey powder is globular protein that is prone to denaturation induced by thermal processing at temperatures above 60°C. One consequence of the protein denaturation is a dramatic reduction in solubility, due to the structural rearrangement of the protein molecule that results in unfolding of the globular structure and exposing the hydrophobic groups that were previously located at the centre regions of the molecule to the outside surface. Protein solubility can thus be used as an indicator of the denaturation.

# 4.4.7.1 Protein solubility measurement method

# 4.4.7.1.1 Solution preparation

The solution was prepared from mixing 300 g of dry powder with 700 g distilled water, the procedure is described earlier in the section (4.1.2). The solutions are filled into pre weighed centrifugation bottles, then re-weighing the bottles when full, and finally after centrifuging checking the weight of the separated phases as will be seen later.

# 4.4.7.1.2 Soluble/Insoluble fraction determination

The separated concentrate solution was decanted from the bottle, and weighed  $(M_{net})$ . The insoluble fraction remaining in the bottle was also weighed and recorded. This was dried in a drying oven at 60 °C for up to 24 hours. A final (dried) sample mass was then determined  $(M_{dry})$ . The ratio of soluble to insoluble protein was calculated using the method described below.

As the insoluble protein mass contained some water that would contain some dissolved native proteins within, would taken into account. It is assumed that this water contains sample concentration of soluble protein as the water initially decanted. In a 100 grams of solution

Whey protein powder	30	g
Deionised water	70	g
If the actual insoluble mass is	x	g
Then the soluble mass is	30 - x	g

The mass fraction of the soluble protein in water is thus measured from

$$\frac{30-x}{70}$$
 Eq (4- 13)

The mass  $(M_{net})$  comprises three components

$$M_{net} = x + w + s \qquad \qquad \text{Eq (4-14)}$$

Where w = Mass of water,

s = Trapped soluble protein which is equal to

$$s = w \left(\frac{30 - x}{70}\right)$$
 Eq (4-15)

The measured mass  $(M_{dry})$  is assumed to have the same quantity of protein but no water, and thus substituting the net and dry masses yield w

Thus

$$M = x + w + w \left(\frac{30 - x}{70}\right)$$
 Eq (4-17)

$$M = x + w - x \left(\frac{w}{70}\right) + w \left(\frac{30}{70}\right)$$
 Eq (4-18)

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$$M = x \left( 1 - \frac{w}{70} \right) + 0.429w + w$$
 Eq (4-19)

$$x = \frac{M - 1.429w}{1 - \frac{w}{70}}$$
 Eq (4- 20)

#### 4.4.7.1.3 Kjeldahl Nitrogen Measurement of NSI

The nitrogen content of the protein was determined using "Buchi Nitrogen Determination System". The analysis is based on measuring the nitrogen content in a known sample mass. The standard procedure of sample digestion, distillation, and titration depends on the equipment used and the principle is explained in AOAC official testing method manual (1998). Kjeldahl method is a nitrogen content measurement method (AOAC 991.20 and 991.22), that's determine the nitrogen content is a % value which is then multiplied by the whey protein content nitrogen factor (6.38) (Fox 1982). The calculation of the protein content from this analysis method is illustrated in equation 18 and 19.

$$N\% = \frac{1.4013 \times \{Vol._{sample \ titeration} \ (ml) - Vol._{blanck \ titeration} \ (ml)\} \times Concentration_{titeration \ acid} \ (M)}{Sample \ Mass} \qquad Eq \ (4-21)$$

Protein  $\% = N \% \times 6.38$ 

#### 4.4.7.2 Measurement procedure of the protein denaturation

After the concentrate preparation, the sample first and the separate the soluble material (presumable native protein), from the insoluble (denatured proteins). The soluble protein is then processed and analysed, see the illustration diagram in figure 4.10. The analysis are carried for determining the level of drying processing effect on the protein stability between the spray drying, rapid spray freeze-drying, and spray freeze-drying. Each sample is had two repeats and the average is taken for the calculated protein content.

Eq (4-22)



Figure 4-16: Flow plan of the whey protein concentrate preparation, processing and testing for denaturation.

#### 4.4.8 Scaning Electron Microscopy (SEM)

SEM is a widely used instrument to probe the microstructure of materials, and thus can be used as post-processing measurement to used relate processing conditions on material product micro-structural properties, and behaviour. In particle structural analysis SEM provides information relating to topographical features, morphology, compositional differences, crystal structure and orientation.

In SEM an electron beam is generated by an electron gun and accelerated to moderately high energy and positioned onto the sample by electromagnetic fields. These beam electrons interact with atoms in the specimen and generate a signal. The signal intensity is mapped and amplified to construct an image.
In contrast to optical microscopy, SEM is not dependent on optical lenses for image formation, instead it uses the principle of electron beam demagnification to focus on the sample surface, to obtain a range of magnification of up to 150000 times and produce depth of field information to give the image three-dimensional appearance. The resolution obtained by SEM is far advanced to that of the optical microscope (Chandler *et al.* 2000).

Here, the SEM method for studying the structure of the frozen states achieved in this freeze and drying processes. The impact of processing conditions on product morphology can then be assessed. The samples collected for SEM analysis were collected immediately at the end of the drying process and their temperature neutralised closed to ambient.

The structural study of biological and volatile materials require special preparation to eliminate the water content in the samples. There are two different methods of spray freezing first spraying ain gaseous freezing medium and the second samples spray froze in liquid nitrogen (cryogenic freezing). Since the samples are placed in vacuum chamber for the SEM imaging they would sublime, hence freeze-dried. Therefore we could perform the SEM imaging on the spray frozen particles. The spray-frozen samples were collected directly from spray operation and placed in container that is pre-cooled and stored in cold space till the analysis. The samples were placed in sealed polycarbonate containers until the moment of testing. The SEM has a limited dimension of sample chamber and the specimen must be affixed to a stage holder for orientation and manipulation within the chamber. Small masses of these particles were adhered to the disc shaped holder by conductive adhesives with a low vapour pressure. This disc was placed in the sample chamber of the SEM instrument at ambient temperature and three images were taken at different magnifications. The relatively low-resolution magnification image first showing the integration of the particulate bulk, the second was for a close visualisation of the bulk integration (fractures and shrivelling of the particles, etc.), and the final image zoomed in on a single particle to display the microstructure of the particles.

The Scan Electron Microscope used in this analysis was Cambridge Stereo Scan 360 UK. Images taken by Mr. Frank Page from the Loughborough Materials Characterisation Centre (LMCC) in the "Institute of Polymer and Material Engineering (IPTME) Department" – Loughborough University.

# Chapter 5

# Spray and Spray Freezing Characterisation - Phase Doppler Anemometry (PDA)

# 5.1 Introduction

The first stage of any spray freeze-drying process is freezing of the spray, whereby the liquid feed is atomised and then frozen, either, by contact with a cold gas, or, a cold liquid. Spray freezing is critical to the success of the SFD process for a number of reasons:

- 1. The particle distribution of the final freeze-dried product is largely determined by the atomisation stage of the spraying process. As well as obviously affecting the form of the final product, this also heavily influences the operation of the drying stage. The smaller particles will dry faster but will also limit the flow rate of drying gas if a fluidised bed is used. A wide distribution will therefore give rise to operational difficulties in the respect that the gas flow rate will be limited by the smallest particle and the drying time limited by the largest particles.
- 2. The rate of freezing of the particles will influence the size and the shape of the ice crystals that form when the particles are frozen. This will affect the morphology of the final dried particle. The distribution and connectivity of the pores left behind by the sublimed ice crystals will be a key feature of the product morphology (and hence functionality) and will also influence the drying rate.

The atomisation process, droplet disintegration, is affected by liquid viscosity, surface tension, atomisation pressures, and nozzle characteristics (Marshall 1954; W.R. Marshall 1954; Masters 1991; Schick 2004). The physical properties of the environment surrounding the nozzle orifice also contributes to the droplet formation, since the atomised liquid disintegrates into ligaments that then break up into droplets due to shear forces created from the contact with the surrounding gaseous environment (Marshall 1954; Perry *et al.* 1997; Richardson *et al.* 2002). These properties will differ under freezing and ambient operation temperatures. For example during spray freezing lowering the operation temperature will increase the liquid viscosity and ice nucleation and crystallization may also affect liquid disintegration.

It is thus important to understand the spray atomisation process, and this is the purpose of this research described in this chapter. The technique used in this research is the "Phase Doppler Anemometry (PDA)" technique, which can measure simultaneously the size and velocity of droplets passing through a small measurement volume. This technique has been used for four main purposes

- i) Measurement of particle size distribution for different nozzles both pneumatic and hydraulic using pure water under different atomisation conditions, e.g. feed pressures. Characterising the spray from these nozzles allows one to choose operational conditions which minimise the spread of the droplet size distribution.
- ii) Investigating the influence of dissolved solutes, sucrose and coffee on the particle size distributions obtained.
- iii) Investigate the potential of the PDA method as a probe for droplet freezing which would be a novel technique.
- iv) Use combined velocity and diameter measurements to fully understand the freezing conditions experienced by different size droplets, and use these data to assess the validity of simple models of the spray freezing process.

Therefore, the study progressed into two parts; (i) a PDA spray study at ambient temperatures on first water and then viscous liquids, and (ii) a PDA study of water sprays at sub-ambient temperatures to allow in comparison to those at ambient temperature.

# 5.2 Phase Doppler Anemometry (PDA)

Laser Doppler Anemometry (LDA) and Phase Doppler Anemometry (PDA) are single point optical diagnostic techniques. The LDA technique is able to measure the instantaneous velocity of individual drops or particles. PDA is an extension of the LDA method and provides an additional measurement of diameter for each droplet/particle (Bachalo *et al.* 1984; Wigley *et al.* 1999; Albrecht 2003). The PDA method can thus measure the following

- Droplet / particle velocity and size
- Droplet / particle trajectory (2D velocity)
- Droplet / particle concentrations
- Droplet / particle velocity to size correlations
- Droplet / particle refractive index, from which density and temperature may be inferred.

These methods of characterisation are used widely in scientific fluid mechanics research activities and industrial process optimisation related to particle streams and liquid sprays. Popular applications include the analysis of atomised liquids in fuel injection systems in internal combustion engines (Wigley *et al.* 1999), pharmaceuticals (Wigley *et al.* 2002), and spray drying flow pattern studies (Southwell *et al.* 2001). A complete PDA unit consists of a laser transmitting unit, receiving optics, signal processor, a PC equipped with an interface board for processing, data acquisition software, and data storage.

The Doppler effect is the main phenomena behind the LDA and PDA techniques. The light scattered by a droplet moving through a laser beam will be Doppler shifted in its frequency. Unfortunately, the frequency of light is so high,  $\sim 10^{14}$  Hz, that there are no electronic photo detectors or frequency analysers that can function. In practice, two laser beams, derived from the same laser so that they are coherent, are crossed The light scattered by a droplet moving through the beams' crossover can be detected by producing a Doppler difference frequency, of the order of  $10^6$  to  $10^8$  Hz, which is directly proportional to the droplet velocity. In general, the 'Fringe Model' is used to describe the LDA and PDA technique. It is considered that when the two beams cross their wavefronts interfere with each other to produce a well defined fringe pattern. Droplets moving through the fringe pattern scatter light with a characteristic burst of sine waves whose amplitude is modulated by a Gaussian distribution representing the <u>intensity distribution across the laser beam. The frequency of the sine waves is measured and An Investigation of Spray-Freezien & Spray-Freeze-Drying</u>



is related to the droplet velocity via the fringe spacing in the crossover.

Figure 5-1: Refraction of light rays through a moving droplet.



Figure 5-2: LDA/PDA Signal generation sequence of spray characterisation, (Wigley 2000).

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Information as regards the droplet size is encoded in the intensity of the scattered light,  $I_{scatterd} \alpha$  diameter<sup>2</sup>. However, this method of sizing is rarely accurate in sprays of industrial importance. An extension of the Fringe Model can be used to show how droplet size can be measured. In figure (5-1) a droplet is shown moving downwards through a fringe pattern. The light rays, forming the fringe pattern, are refracted as the droplet moves vertically through. If two detectors are placed in the vertical plane, either side of the horizontal axis through the fringe pattern, they will each generate a burst of sine waves as the refracted light is intercepted. However, there will be a time delay between the two bursts which is related to the radius of curvature of the droplet. As the signal processor measures the sine wave frequency it also measure the time difference as a 'phase difference' between the two bursts.



Figure 5-3: Different light scattering mode caused by a drop passage. (http://www.dantecmt.com/).





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The fringe spacing  $D_f$  is a function of the intersection angle,  $\theta$ , and wavelength  $\lambda$ ,

$$D_f = \frac{\lambda}{2\sin\frac{\theta}{2}} \qquad \text{Eq (5-1)}$$

A droplet or a particle passing through the measurement volume will scatter light by refraction and reflection. This produces a signal with a sinusoidal oscillation frequency of  $F_d$ , for the duration of the droplet transit time through the measurement volume. The droplet/particle velocity V is determined by equation (5-2).

$$V = F_d D_f Eq (5-2)$$

The scattered light is picked up by a receiver unit, which are organised in a symmetric y and z plane in relation to the measuring volume and houses between 2 and 5 detectors depending on the velocity components measured. They are arranged at an angle  $\pm \Psi$ . The PDA instrument is provided with two photo detectors. Here the drop traversing through the measuring volume generates what is known as a Doppler burst of the same frequency sweeping the two detectors, figure (5-4), but the two bursts have a phase difference according to the elevation angle of detector position ( $\Psi$ ). The light intensity is also not uniform and depends on the refractive index of the drop ( $n_{rel}$ ). The beams intersecting angle ( $\theta$ ) and the wave scattering from drop interference in the fringe volume has an angle ( $\varphi$ ), see figure (5-4). The difference between the two bursts depends on the drop size and the spatial frequency of the interference fringe pattern and is proportional to the drop diameter.

$$n_{rel} = \frac{n_{particle or drop}}{n_{medium}} = \frac{n_P}{n_M}$$
 Eq (5-3)

The droplet diameter D is derived from the phase difference  $\Phi$  between the signals from the two detectors it is mathematically represented by the following equations, which is a function of the geometry as seen in equations (5-4) and (5-5), (Dantec Measurement Technology 2004). For reflection:

$$\Phi = \frac{2\pi d_p}{\lambda} \frac{\sin\theta \sin\psi}{\sqrt{2(1 - \cos\theta \cos\varphi \cos\psi)}}$$
 Eq (5-4)

For 1<sup>st</sup> order refraction:

$$\Phi = \frac{2\pi d_p}{\lambda} \frac{n_{rel} \sin \theta \sin \psi}{\sqrt{2(1 + \cos \theta \cos \psi \cos \varphi)(1 + n_{rel}^2 - n_{rel})\sqrt{2(1 + \cos \theta \cos \psi \cos \varphi)}}}$$
 Eq (5-5)

The angular positioning of the receiver compared to the incident beam can be carefully selected to maximise or minimise each type of scatter leading to the domination of one type of scattered light.

A schematic of the LDA/PDA transmitter system used in this research is shown in figure (5-5). Two beams of equal intensity exit the Bragg cell, symmetrically about the optical axis, with an angular separation of 1.88 degrees. The first order diffracted beam is frequency shifted by +40 MHz and has an orthogonal polarization direction to the zero order beam. The laser beam expander, lenses (7) and (8), expand and collimate these diverging beams to produce a beam separation of up to 50 mm with an expanded beam diameter of 4.4 mm. A second half-waveplate (5) is then required to match the shifted and input beam polarization directions. The Bragg cell and beam expander lenses are integrated into a single optomechanical unit 300 mm long.

The beam separation control is a simple translation of the Bragg cell, along the optical axis, followed by a small refocus of lenses (9) and (8) to achieve collimation of the beams. The three element front lens (9) focuses the two beams to form the diffraction limited measurement volume (10).



Figure 5- 5: Laser and Phase Doppler Anemometer System.

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For two colour operation, 488 nm (blue) and 514 nm (green) wavelengths, the prisms (1) are replaced by Pellin Broca dispersing prisms and the components (3) to (8) have to be duplicated with the second Bragg cell and half-wave Plate rotated through 90 degrees. The orthogonal blue and green beam pairs would be combined on the optical axis before the front lens (9), (Pitcher *et al.* 1994). This is not seen as an unnecessary complication due to the high degree of flexibility offered since the variable beam expanders can be set to:- (a) equalise the beam separation for each wavelength, (b) equalise the dimensions of the two measurement volumes or, (c) create unequal measurement volume diameters with one inside the other.

The specification for the beam diameter at the front lens and the measurement volume dimensions are given in the LDA/PDA operational parameter list. These have been calculated using Gaussian beam theory but substituting the equivalent single thin lenses for the complex optical geometry of the beam expander.

#### **LDA/PDA operational parameters**

Transmitter					
Laser Wavelengths	514 nm	488 nm			
Laser Powers - Low	250 mw	120 mw			
Laser Powers - High	300 mw	150 mw			
Beam Separation	50 mm	50 mm			
Beam Width	5.0 mm	5.0 mm			
Focal Length	450 mm	450 mm			
Measurement Volume Diameter	59 µm	56 µm			
Fringe Spacing	4.64 μm	4.40			
Number of Fringes	13	13			
Light Polarization	Parallel to Fringes	Parallel to Fringes			
Receiver (Classic)	D	antec 57X10			
Scattering Angle	70 Degrees				
Lens Focal Length		500 mm			
Measurement Volume Length		110 µm			
Aperture / Max. Dropsize	0.5	mm / 233 μm			
Photo-multiplier voltage - low		816 volts			
Photo-multiplier voltage - high	952 volts				
Processor					
Bandwidth / Gain	45	5 MHz / Low			
Velocity Bandwidth	-46 to 160 m/s				
Validation					
Signal Level / Velocity		Yes			
Validation Level	0 dB				
Diameter / Spherical		Yes			
Phase error		10 degrees			
Spherical Deviation		10 %			

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The measurement volume dimensions refer to the  $TEM_{00}$  Gaussian beam diameter at the  $1/e^2$  points. These dimensions are seen as the minimum since use of the inter-cavity aperture actually reduces the output laser beam diameter and will therefore increase beam waist dimensions. It is the specific requirement for this mode that limits the output power of the Argon-Ion laser.

Due to the availability of just one receiver unit it was decided to perform the experiment with the receiver positioned to maximise the signal from refractive scattering. This would enable velocity and size measurement to be made of the liquid drops, which scatter light predominantly by refraction. This was judged to present the most reliable data as the experiments could first be tested at ambient temperatures. One of the areas of enquiry of this research was examining whether the PDA technique, which is sensitive to the type of scatter and thus also theoretically the phase state of the droplet / particle, could thence be used as a probe to discriminate whether freezing was taking place in an individual droplet.

# 5.3 Experimental methods

#### 5.3.1 Apparatus and materials

The liquid materials used in this spray characterisation analysis were distilled water, 30% (*w/w*) aqueous sucrose solution, and 30% (*w/w*) aqueous coffee solution concentrate. The related physical and optical properties of these liquids are described in Chapter 4, section 4.2.6.

The hydraulic and pneumatic nozzles used in this research were previously described in chapter 3.

A spray freezing chamber constructed for this work was described in Chapter 3. The cylindrical section chamber had 5 thermally-toughened glass windows, 1000 mm long, 144 mm wide, and 10mm thick to allow PDA and imaging experiments to be made. These windows designed to be swiftly removed for cleaning purposes. In practice three windows were used in this spray characterisation experiments, see figure (5-6). The general set up of the measuring spray characterisation rig and chamber is shown in figure (5-7). The spray measurement tests were performed in both ambient and sub-ambient temperatures.



Figure 5-6: PDA measurement arrangement on the windows in the chamber (plan 1view).



Figure 5-7: Side view illustration of the PDA set up inside the chamber.

#### 5.3.1.1 Ambient spray environment

PDA spray characterisation experiments at ambient temperature were carried out under stagnant or flowing gas stream conditions. The latter was produced by the suction from a vented gas outlet see figure (5-7). One of the closed windows was replaced with a wooden board of the same window dimension, but with 100 mm diameter opening at the top of this board was placed to act as ambient air inlet. The flow velocity was controlled by adjusting the extraction power at the outlet point until the gas velocity at the outlet (measured by a hand held rotary vane velocity meter) corresponded to average value of either 1.5 or 5 ms<sup>-1</sup>. Experiments performed with zero gas inlet flow were termed as "stagnant or no flow", however this is not intended to imply that there was zero flow inside the chamber.

#### 5.3.1.2 Sub-ambient spray environment

For experiments at sub-ambient temperatures the chamber was first purged with nitrogen gas for 5-10 minutes. This was necessary to reduce the humidity present inside the chamber, which would cause immediate fogging when the chamber was cooled. The nitrogen gas was first supplied from a compressed gas cylinder, subsequently, a small flow of liquid nitrogen was introduced into the chamber begin to slow cooling and avoid thermal shock. The large volume of the chamber has a significant heat capacity, of both air volume and the metal wall, in order to cool the chamber within a reasonable time frame it was necessary to introduce liquid nitrogen directly into the chamber. This typically took up to 10 minutes for the chamber wall reach  $\pm$  5°C, the target spray freezing operation temperature. Thereafter, the nitrogen gas flow was controlled to maintain the operating temperature and gas velocity, by regulating the ratio of LN<sub>2</sub> and cylinder N<sub>2</sub> gas flows. The gas velocity was measured in a similar way for the ambient experiments operation. Here the main driving force for the gas flow was regulating the LN<sub>2</sub> dewer and N<sub>2</sub> cylinder valves rather than suction from the exhaust vent.

#### 5.3.1.3 PDA data acquisition

Spray characterisation requires high visual clarity in the measurement space and spray stability in the chamber. The configuration for this application was described in section 5.2., the spray characterisation measurement was carried out with the help of Dr. G. Wigley carried.

The setup is described as follow:

- The laser was switched on at least one hour prior to testing to allow stable operation and measurements.
- Depending on the clarity inside the chamber either the dual beam (green and blue beams) or single colour beam (green) was selected. The single beam method of measurements was used for poorer visibility operations.
- The laser beam powers were set to the intensity (120-300 mW) depending on the measurement conditions, vision clarity, inside the chamber.
- For the ambient temperature experiments the photo detection voltage was 816 volt, which was increased to 952 volts in sub-ambient conditions when required.
- The whole PDA system was scanned in the vertical plane. However the measurement volume to an axial point in the chamber.
- The atomisation pressures were set prior to PDA by performing a trial spray and adjusting the feed valves as necessary.
- The spray chamber was prepared to the required operating temperature and maintained at a steady values (see previous sections).
- The spray is commenced and data acquisition occurred after a few seconds to avoid initial transient behaviours. Data acquisition typically lasted 3 seconds.
- At the end of the test all valves were shut off and the liquid feed to the atomiser flushed with pressurised nitrogen gas to remove empty any residues. This was particularly important for sub-ambient operations in order to prevent nozzle from freezing.

The spray appears, from visual observation, to travel up to 1 m inside the chamber beneath the spraying point before it appears to becomes turbulent, at least for first 2-3 seconds. The vision clarity inside the chamber is maintained for 5-8 seconds maximum, thereafter the turbulent mist formed hinders the laser beam transition. There practical difficulties due to the turbulent development of the spray entrainment, and hence cloud formation required the PDA testing to have a manual override for the measurement end time in addition to the automatic setting of a fixed measurement elapsed time or droplet data population collected.



Figure 5-8: Photograph of the spray freezing chamber and PDA equipment during an experiment.

- 1) laser source,
- 2) laser transmitter,
- 3) input laser beam,
- 4) measurement volume,
- 5) PDA receiver,
- 6) signal processor,
- 7) spraying chamber,
- 8) spray nozzle inside a holder, and
- 9) chamber gas inlets.

# 5.3.2 Mathematical representation of the spray measurement

The data analysis concentrated on two main measurements for each spray. The first was the spray size distribution and the second was to correlate the real time droplet velocities to the droplet diameter range of the spray. This method of analysis and presentation are now described.

# 5.3.2.1 Drop/Particle size distribution

Drop size distribution data are best presented graphically in the form of a probability distribution function, PDF, whereby the frequency of drops given in a size interval is plotted against particle size. This is expressed mathematically by:

$$f_i = \frac{n_i}{N} = h_i \Delta d_i \qquad \qquad \text{Eq (5-6)}$$

$$\sum f_i = \sum (h_i \Delta d) = 1$$
 Eq (5-7)

fi	= fraction drops in size interval bin $(i)$	
d	= drop or particle diameter	
n <sub>i</sub>	= number of drops in size interval $(i)$	
N	= total number of drops	
h <sub>i</sub>	= height (as fraction) of drop size $(d_i)$	
$\Delta d$	= interval size (1 $\mu$ m in this research).	

The data can also be processed to produce mean diameter values that can be used to characterise the distribution, as seen in table 5-1. There are different terminologies describing the calculation for drop size of spray population, they were based on the interest of the study, or process. A complete drop size and characterisation terminology can be found in ASTM standard E1296-92 (Marshall 1954; Tishkoff 1984; Schick 2004).

# 5.3.2.2 Method of data analysis

The statistical drop size estimates listed in table 5-1 were calculated for each experiment using "Size 24" loaded on the data acquisition PC. Particle size distribution and velocity profile plots were obtained by first transforming the complete data set (diameter value and corresponding velocity for each drop) to an Microsoft Excel spread sheet. Typically 200000 droplets, or an acquisition time 2 seconds, was used for the pneumatic nozzles, which ever

was exceeded first. For the hydraulic nozzle spray the droplet count was reduced to approximately 5000 or for a data acquisition time 60 seconds.

For some experiments, involving a twin fluid nozzle, this typically required importing the data to four work sheets, within a single workbook, as the number of rows in a worksheet is limited to 65,536. The particle size distribution heights  $(h_i)$  were calculated using the Excel frequency function. The average velocity  $(v_i)$  in each interval and the sum of the square of the velocities in each bin, to be used in equation 5.9, were calculated using a Visual Basic script linked to the Excel workbook.

#### 5.3.2.3 Velocity profiling of the drops measured in the spray

The drop field in each spray have a characteristic velocity profile that is related to the nozzle type and drop size. The drop velocity is important in influencing the heat transfer coefficient between the gas and the drops, via the slip velocity, which means that it influences the rate of freezing. Drop velocities will also determine the distance which a droplet travels during the time it takes to freeze.

The PDA measurement of the spray as described earlier can provide up to 3 velocity components of the drops measured, but this research only considered the axial velocity component ( $\nu$ ) as the vertical measurement scan was restricted to the spray axis and both cross components were expected to be zero. Further more, during the sub-ambient temperature work fogging would substantially decrease the probability of 2 component velocity measurements area that give 1 component. A drop inside a spray is subjected to a range of different forces and interactions with other drops, and surrounding flowing gas. These result in a variation in the velocity of drops even those of the same size. This means that, for a single drop range interval ( $\Delta d$ ) we may expect a range of velocities. For this, an average mean velocity and standard deviation can be calculated, from which the mean velocities plotted against the drop size range for each spray. The standard deviation equation used in this calculation is eq (5-9).

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} \left(v_{i} - \bar{v}_{i}\right)^{2}}{n-1}}$$
 Eq (5-8)

which is rearranged into

$$\sigma = \sqrt{\frac{\sum v_i^2 - n \bar{v_i}^2}{n - 1}}$$
 Eq (5-9)

Where -

 $v_i$ 

 $v_i$ 

= is the velocity of  $i^{th}$  droplet in the interval *i*.

= is the average velocity of the droplets in the interval i.

**Table 5-1:** Spray drop characteristic terminology used for the spray freezingcharacterisation(Marshall 1954; Lefebvre 1989; Holdich 2002; Schick 2004).

Parameter	Definition	Application				
$D_{I0}$	Arithmetic or length mean diameter	Evaporation rate				
	$D_{10} = \bar{d} = \frac{\sum d_i}{N} = \sum f d_i$					
D <sub>20</sub>	Surface mean diameter $D_{20} = \sqrt{\frac{\sum d_i^2}{N}}$	Surface controlled phenomena, such as absorption				
D <sub>30</sub>	Volume mean diameter $D_{30} = \sqrt[3]{\frac{\sum d_i^3}{N}}$	Volume controlled phenomena, such as hydrology.				
D <sub>31</sub>	Mean evaporative diameter $D_{31} = \sqrt[3]{\frac{\sum d_i^3}{\sum d_i}}$	Calculation of molecular diffusion, evaporation				
D <sub>32</sub>	Sauter mean diameter (SMD) is the diameter of the drop having the same volume to surface area ratio as the spray as a whole. $D_{32} = \frac{\sum d_i^3}{\sum d_i^2}$	Heat and mass transfer				
D <sub>V0.1</sub>	Droplet diameter where 10 % of the total volume of the spray has a smaller or equal diameter.	Evaluating the nozzle drifting potential.				
D <sub>V0.5</sub>	Volume median diameter (VMD) is the diameter where 50% of the total volume of the spray has a small or equal volume.	A mean of expressing the drop size in term of liquid sprayed				
D <sub>V0.9</sub>	Droplet diameter where 90 % of the total volume of the spray has a smaller or equal diameter.	Required to evaluate the completion of spray evaporation				
RSF	Relative span factor is a dimensionless parameter. It is calculated from $RSF = \frac{D_{V0.9} - D_{V0.1}}{D_{V0.5}}$	Indicating the uniformity of drop size distribution				
D <sub>32</sub> /D <sub>10</sub>	Dimensionless parameter	Can be used as a measure of size uniformity. (1 = perfectly uniform).				

# 5.4 Ambient spray characterisation

# 5.4.1 Introduction

This set of spray measurements were undertaken at ambient temperatures. A preliminary series was made using distilled water to assess operational conditions for the drop size uniformity. This was followed by an experiment with more viscous feeds, sucrose concentrate and coffee concentrate, to assess the effect of the composition on the spray characteristics.

# 5.4.2 Water spray characterisation

The design of a spray freezing and drying process requires knowledge of the particle size of the materials handled in the operational units. In the spray freezing operation a narrow size distribution of the spray is an ideal scenario for the uniformity of freezing times and quality enhancement by processing at optimal conditions for all particles. These particulates then forwarded to the fluidisation vessel that requires a particulate bulk of even size distribution for the purpose of uniform sublimation and fluidisation properties. Since the spraying operation is the first processing stage in the spray freeze-drying chamber proposed in this research it is a necessity to have a reasonably narrow drop/particle size distribution production of the material bulk for adequate modelling and designing for optimal efficiency.

The main objectives of this PDA spray characterisation experiment was to measure the drop size distribution of the sprays in relation to variation of the feed pressure and nozzle types in order to gain an understanding of the operation capacity and setup of these nozzles and choose the optimal atomisation conditions for the good particle size production for later experiments. A further investigation was made of the effect of the chamber gas flow on the produced spray size distribution.

Three spray nozzles were used in these experiments; these were the XA Pr, SAM, and WL made by BETE Ltd

 XA Pr Pneumatic: full cone internal mixing spray nozzle with two assemblies; the Pr 050 and Pr100 assemblies. They differ in the type of air cap of the nozzle, most notably the orifice of the air cap in the Pr100 was larger for Pr 050.

- <u>SAM Pneumatic:</u> full cone external mixing with (optional fan) spray nozzle with two assemblies (SAM-01-02) and (SAM-02-02). The difference between these two assemblies is that the fluid cap in the SAM 02-02 was larger orifice than that of the SAM 01-02.
- 3. <u>WL 0.25 hydraulic:</u> a full cone spray nozzle with an orifice diameter of 1.09mm.

It was planned to test all the nozzles and available assemblies with a range of atomisation gas and liquid feed pressures and also studying the effect of the chamber gas flow on the spray. The experimental plan is illustrated in figure (5-9); the following conditions were used:

- The liquid supply to the nozzles was distilled water
- The atomisation gas used for pneumatic atomisers was compressed nitrogen gas.
- The temperature inside the spray-freezing chamber was 18-22 °C.
- All experiments were carried for both stagnant and ambient flowing air conditions,
   0 and 1.5 ms<sup>-1</sup> for pneumatic nozzles, 0, 1.5 to 5 ms<sup>-1</sup> for the hydraulic nozzle.
- Characterisation by 2 components PDA measurements techniques (blue & green laser).
- The PDA measurement point was 60 mm vertically below the nozzle orifice.

# 5.4.2.1 Results of the water spray experiments

The SAM nozzle had the capability to produce a fan sheet spray as well as cone spray. It was an interesting option to measure the size distribution spray in the fan sheet, as this would have lead to a unique freezing environment for future work with sub-ambient temperatures. Therefore the SAM (01-02) nozzle was tested in a fan sheet mode at pressurised feeds of 1 bar gas + 1 bar liquid and 1 bar fan sheeting gas. This spray developed a highly turbulent flow pattern inside the chamber almost instantaneously that caused immediate fogging which prohibited any spray measurement. This nozzle mode was thus rejected for further experiments.

A summaries of the PDA data from the measured spray nozzles are listed in tables (5-2) to (5-5), and graphical representations of the drop size distributions are shown in figures (5-10) to (5-15). The results exhibit variation in spray features between the nozzles, demonstrating the characteristic difference in atomisation and spray velocity. The tables indicate two parameters of "attempted" and "validated" samples. The first, attempted samples, represents the number of drops passing through the measurement volume and generate a signal detected by the signal processor. The second, validated samples, represents those drops which were successfully measured (for diameter and velocity) by the PDA equipment. The main criteria of sample validation by the processor is based on the droplet sphericity. The validated are thus a subset of the attempted samples.



Figure 5-9: The nozzle operation plan for the preliminary experiment.

The number of the attempted samples per unit time detected in the PDA measurement volume was variable between the sprays as indicated in tables 5-2 to 5-3. The tables also indicated the *An Investigation of Spray-Freezing & Spray-Freeze-Drying* 173

rate of data collected is related to the droplets velocities as well as the time duration of measurement, the higher the droplet velocity the higher the data rate gathered in a shorter time.

# 5.4.2.1.1 Results for the XA pneumatic nozzle

This nozzle produced a very fine spray wit a large population and a narrow drop size distribution, DSD. A statistical analysis of the spray is summarised in table (5-2) and the droplet size distributions are shown in figures (5-10) and (5-11). They indicate the behaviour of this nozzle performance in relation to the feed pressure variations as well as effect of the spraying environment, for both nozzle assemblies. The main results can be described as follows:

# Effect of feed pressure variation

- The mean vertical velocity of the drop flow in the sprays is approximately proportional to the atomisation gas feed pressure, the spray mean velocity increased by approximately 50%.
- An increase in the liquid feed pressure, from 1 bar to 2 bar, at a constant gas pressure resulted in an increase in the spray DSD as the values of D<sub>v0.9</sub> increased 3 to 4 times, while the velocity increase is insignificant. This may be the results of the increase in the liquid feed flow rate.
- Increasing the atomisation pressure of both liquid and gas feed, test 3 for both assemblies, in equal proportions had little influence on the DSD of the spray. However, increasing only the liquid feed increased the breadth of the DSD.

#### Effect of chamber gas flow rate variation

- The results in figure (5-10) shows only a small effect of the chamber gas conditions on the drop size distribution from the XA Pr050 nozzle. A slightly more pronounced decrease in its drop size distribution was observed with the Pr100 assembly, as the spray mean diameter size shifted toward the smaller sizes figure (5-11).
- The spray mean velocity is slower in the flowing gas for sprays at equal gas to liquid feed atomisation pressures, however the ratio is not consistent as this mean velocity is dependent on the number of drops and analysed and their velocity.

# Nozzle assembly

- The mean spray velocity increased by a factor of approximately 25% in the Pr 100 in comparison to that of Pr 050, table (5-3).
- The mean spray diameters of each spray conditions for the Pr 100 assembly spray seems to be larger by 1-2  $\mu$ m in comparison to the corresponding spray from the Pr 050 nozzle assembly.
- There is no noticeable difference when comparing the RSF values for the two nozzle assemblies.

XA pr50								
	1bar gas +	1bar liquid	1bar gas +	2bar liquid	2 bar gas + 2bar liquid			
	Stagnant	Flowing	Stagnant	Flowing	Stagnant	Flowing		
	air	air	air	air	air	air		
Attempted Sample no.	111348	166844	169117	168993	169532	170589		
Validated Sample	100118	150154	150448	150424	150207	150351		
Data Rate (kHz)	97.383	60.874	56.090	54.057	121.170	143.925		
Elapsed Time (s)	1.14	2.74	2.97	3.13	1.40	1.19		
Mean Vertical Velocity (ms <sup>•1</sup> )	45.61	40.11	32.25	33.76	63.06	60.85		
D <sub>10</sub> (μm)	10.58	9.86	14.62	14.78	10.83	10.09		
D <sub>20</sub> (μm)	11.78	11.01	16.98 17.04		11.70	11.08		
D <sub>30</sub> (µm)	13.07	12.23	20.44 20.06		12.63	12.13		
D <sub>31</sub> (μm)	14.53	13.62	24.16	23.37	13.64	13.30		
D <sub>32</sub> (SMD) (μm)	16.08	15.09	29.61	27.78	14.71	14.54		
D <sub>V0.1</sub> (μm)	9.72	9.00	15.03	14.92	9.35	8.98		
D <sub>V0.5</sub> (VMD) (μm)	17.99	17.23	35.99	32.34	15.66	15.79		
D <sub>V0.9</sub> (μm)	29.38	26.12	100.41	79.29	25.55	26.00		
$D_{32}/D_{10}$	1.52	1.53	2.03	1.88	1.36	1.44		
RSF	1.09	0.99	2.37	1.99	1.03	1.08		

 Table 5-2: Summary data of water sprays produced by the XA (Pr050 and Pr100) pneumatic nozzle at ambient temperature.

XA pr100									
	1bar gas +	1bar liquid	1bar gas +	2bar liquid	2 bar gas + 2bar liquid				
	Stagnant	Flowing	Stagnant	Flowing	Stagnant	Flowing			
	air	air	air	air	air	air			
Attempted Sample no.	169822	167524	175588	176207	181963	180340			
Validated Sample	150276	150174	150714	150794	150632	150531			
Data Rate (kHz)	119.378	97.727	58.425	68.092	113.870	175.106			
Elapsed Time (s)	1.42	1.71	3.01	2.59	1.60	1.03			
Mean Vertical Velocity	62.22	50.51	20.02	20.02	70.40	70.60			
(ms <sup>-1</sup> )	05.22	52.51	39.92	59.05	/ 6.46	79.00			
D <sub>10</sub> (μm)	12.83	11.48	16.69	16.69 15.49		11.15			
D <sub>20</sub> (μm)	13.93	12.79	19.46 18.09		15.18	12.14			
D <sub>30</sub> (μm)	15.11	14.11	23.69	21.96	16.24	13.19			
D <sub>31</sub> (μm)	16.41	15.65	28.22	26.15	17.35	14.34			
D <sub>32</sub> (SMD) (µm)	17.79	17.19	35.08	32.34	18.57	15.55			
$D_{y_{0,1}}(\mu m)$	11.23	10.71	17.14	16.04	12.19	9.87			
D <sub>V0.5</sub> (VMD) (μm)	19.12	19.17	44.25	40.34	16.65	19.38			
D <sub>V0.9</sub> (μm)	31.31	29.22	122.47	112.69	27.26	31.83			
D <sub>32</sub> /D <sub>10</sub>	1.39	1.50	2.10	2.09	1.31	1.40			
RSF	1.05	0.97	2.38	2.40	1.04	1.01			



Figure 5-10: Normalised size distribution of water spray produced by XA Pr 050 pneumatic nozzle at ambient temperature for both stagnant and flowing air at the following feed pressures (A) = 1 bar gas + 1 bar liquid, (B) = 1 bar gas + 2 bar liquid, & (C) = 2 bar gas + 2 bar liquid.



(C)

Figure 5-11: Normalised size distribution of water spray produced by XA Pr100 pneumatic nozzle at ambient temperature for both stagnant and flowing air at following feed pressures (A) = 1 bar gas + 1 bar liquid, (B) = 1 bar gas + 2 bar liquid, and (C) = 2 bar gas + 2 bar liquid.

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# 5.4.2.1.2 Results for the SAM pneumatic nozzle

This nozzle produced sprays contained droplets that were generally slower and of a larger mean size than for the XA Pr Nozzle. The atomisation performance indicates better control of drop size distribution at different liquid feed pressures. The overall indication from the normalised droplet distribution charts in figure (5-12) and (5-13) shows that the distribution pattern varies little between different operation conditions, however, the calculated mean diameters did vary. The results shown in table (5-3) can be interpreted as follow

# Effect of pressure variation

- Increasing the gas pressure from 1 bar to 2 bar raises the average spray velocity by approximately 30%, and slightly decreases the average drop size ( 50% by various measures).
- Increasing the liquid feed pressure from 1 bar to 2 bar causes a slight increase in spray mean velocity by 6%, the mean size diameter shows insignificant difference.
- Increasing both liquid and gas pressure by a factor of 2 had almost no effect on particle size, but does generate an increase in drop velocity.
- The RSF values for all tested condition of this nozzle atomisation was generally higher than the XA nozzle, indicating a lower degree of atomisation.

#### Effect of chamber gas flow rate variation

• The flow environment appears to have a little effect on the spray characteristics, i.e. the spray distribution representations are not significantly different between the stagnant and flowing air sprays, figure (5-12) and (5-13).

#### Nozzle assembly

- The SAM 02-02 assembly produced a finer and slower atomisation than the SAM 01-02.
- The RSF values have small difference with no comparative order pattern to the matching condition.

SAM S01-02									
	lbar gas +	1bar liquid	1bar gas +	2bar liquid	2 bar gas +	2bar liquid			
	Stagnant air	Flowing air	Stagnant air	Flowing air	Stagnant air	Flowing air			
Attempted Sample no.	_166002	166634	171091	175635	171887	175760			
Validated Sample	150464	150540	150979	151300	150683	150861			
Data Rate (kHz)	50.953	48.248	51.874	51.936	91.238	92.149			
Elapsed Time (s)	3.26	3.45	3.30	3.83	1.88	1.91			
Mean Vertical Velocity (ms <sup>-1</sup> )	31.51	30.44	34.31	32.29	45.51	45.24			
D <sub>10</sub> (μm)	13.28	13.15	13.28	12.58	13.28	13.09			
D <sub>20</sub> (μm)	16.11	16.35	17.32	17.14	16.15	16.28			
D <sub>30</sub> (μm)	20.72	21.36	24.28	25.16	20.64	21.36			
D <sub>31</sub> (μm)	25.87	27.22	32.84	35.58	25.74	27.30			
D <sub>32</sub> (SMD) (μm)	34.27	36.47	47.75	54.19	33.72	36.82			
D <sub>V0.1</sub> (μm)	15.68	16.70	20.11	23.51	15.28	16.40			
D <sub>V0.5</sub> (VMD) (μm)	49.32	53.51	79.87	92.44	54.49	48.94			
D <sub>V0.9</sub> (μm)	135.45	124.86	169.59	176.97	130.58	110.01			
$D_{32}/D_{10}$	2.58	2.77	3.60	4.31	2.54	2.81			
RSF	2.43	2.02	1.87	1.66	2.10	1.94			

Table 5-3: Summary data of water sprays produced by the SAM (S01-02 and S02-02)pneumatic nozzles at ambient temperature.

SAM S02-02									
	1bar gas +	1bar liquid	1bar gas +	2bar liquid	2 bar gas +	2bar liquid			
	Stagnant	Flowing	Stagnant	Flowing	Stagnant	Flowing			
	air	air _	air	ai <del>r</del>	air	air			
Attempted Sample no.	165549	163375	164140	162967	168621	168905			
Validated Sample	150603	150507	150433	150419	150336	150344			
Data <u>Rate (</u> kHz)	28.205	23.424	28.506	24.450	58.261	62.498			
Elapsed Time (s)	5.87	6.97	5.76	6.67	2.89	2.70			
Mean Vertical Velocity (ms <sup>-1</sup> )	21.49	21.29	22.64	21.39	31.02	33.88			
D <sub>10</sub> (μm)	13.00	12.97	12.72	12.54	11.86	11.17			
D <sub>20</sub> (µm)	16.65	16.90	16.19	16.45	14.12	13.41			
D <sub>30</sub> (μm)	22.65	23.07	21.51	22.62	17.37	16.71			
D <sub>31</sub> (μm)	29.91	30.77	27.97	30.38	21.02	20.43			
D <sub>32</sub> (SMD) (µm)	41.91	43.01	37.94	42.79	26.27	25.92			
D <sub>V0.1</sub> (μm)	18.75	19.92	17.92	19.91	13.13	12.44			
D <sub>V0.5</sub> (VMD) (μm)	66.68	66.00	55.99	65.37	32.91	34.01			
D <sub>V0.9</sub> (μm)	150.30	147.58	128.27	141.19	83.39	85.47			
D <sub>32</sub> /D <sub>10</sub>	3.23	3.32	2.98	3.41	2.22	2.32			
RSF	1.97	1.93	1.97	1.86	2.13	2.15			



Figure 5-12: Normalised size distribution of water spray produced by SAM (01-02) pneumatic nozzle at ambient temperature for both stagnant and flowing air at following pressures (A) = 1 bar gas + 1 bar liquid, (B) = 1 bar gas + 2 bar liquid, and (C) = 2 bar gas + 2 bar liquid.

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Figure 5-13: Normalised size distribution of water spray produced by SAM (02-02) pneumatic nozzle at ambient temperature in stagnant and flowing air at feed pressures (A) = 1 bar gas + 1 bar liquid, (B) = 1 bar gas + 2 bar liquid, and (C) = 2 bar gas + 2 bar liquid.

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# 5.4.2.1.3 Results for the WL hydraulic nozzle

The spray produced by this nozzle was characteristic of general hydraulic nozzle performance when compared to the pneumatic sprays. It produced a full cone spray with a wide coverage area, a lower drop population, larger drops (visible to the naked eye) and a wide size distribution. The overall mean velocity is much lower than for the pneumatic nozzle sprays. Therefore, the elapsed time for the PDA measurement was extended to a duration of 60 seconds in order to measure a significant number of drops from the spray. The characteristic atomisation parameters for this nozzle for water vary with the operational pressures and the surrounding environment. The results of table (5-4) summarise these differences.

# The main conclusion were:

#### Effect of pressure variation

- The spray mean velocity increases with pressure by 10 to 15 %.
- Increasing the atomisation pressure increased the liquid disintegration and helped reduces the drop size estimates for  $D_{10}$  and  $D_{32}$ .
- The pressure increase led to increased RSF values for the nozzle, indicated a poorer spray homogeneity.

#### Effect of chamber gas flow rate variation

- The graphical representation of the drop-normalised distribution in figure (5-14) indicates inter-relation between the atomisation pressure and the flowing environment. Spraying in a higher air flow environment helps the liquid disintegration thence reducing the values of the arithmetic and Sauter mean diameters as seen in the sprays produced at 1.5 and 5 m/s flowing gas.
- Increasing the air flow conditions increases the spray population.
- The relative span factor, RSF, of the nozzle performance shows atomisation enhancement for the spray in the flowing environment more than into stagnant air.
- The drop size distribution for the spray in stagnant air is much flatter than in flowing gas, i.e. a relatively flat distribution of the sizes especially up to  $100\mu$ m.

WL0.25									
	3.5 bar liquid			4.5 bar liquid			5.5 bar liquid		
Spraying environment (ms <sup>-1</sup> )	Stagnant air	Flowing air ~ 1.5	Flowing air ~5	Stagnant air	Flowing air ~ 1.5	Flowing air ~5	Stagnant air	Flowing air ~ 1.5	Flowing air ~5
Attempted Sample no.	23429	19274	12473	31825	33166	18621	43157	47330	25920
Validated Sample	16096	11522	8258	23562	22737	13797	35077	34676	20899
Data Rate (kHz)	0.39044	0.32121	0.41567	0.53041	0.55269	0.62069	0.71927	0.78883	_0.86399
Elapsed Time (s)	60.01	60.00	30.01	60.00	60.00	30.00	60.00	60.00	30.00
Mean Vertical Velocity (ms <sup>-1</sup> )	12.96	12.82	13.38	14.48	14.91	15.13	17.15	16.69	16.82
D <sub>t0</sub> (μm)	83.83	71.75	63.81	75.72	56.37	54.77	69.74	48.50	48.21
D <sub>20</sub> (µm)	98.48	88.87	80.79	89.50	72.02	70.59	81.79	63.22	63.04
D <sub>30</sub> (µm)	110.30	102.83	94.98	100.96	85.60	84.63	92.24	76.53	76.57
D <sub>31</sub> (μm)	126.52	123.10	115.89	116.58	105.49	105.19	106.09	96.14	96.49
D <sub>32</sub> (SMD) (μm)	138.36	137.65	131.30	128.47	120.95	121.63	117.31	112.15	112.97
D <sub>V0.1</sub> (μm)	94.31	86.34	91.63	85.63	78.18	78.68	77.03	72.51	71.56
D <sub>V0.5</sub> (VMD) (μm)	158.22	160.93	153.78	146.48	142.40	145.17	132.46	133.81	134.23
D <sub>v0.9</sub> (μm)	210.65	213.94	209.76	203.67	203.28	210.27	195.97	197.34	_200.73
$D_{32}/D_{10}$	1.65	1.92	2.06	1.70	2.15	2.22	1.68	2.31	2.34
RSF	0.74	0.76	0.80	0.81	0.88	0.91	0.90	0.94	0.96

 Table 5-4: Summary data of water sprays produced by WL0.253 hydraulic nozzle at ambient temperature.



Figure 5-14: Normalised size distribution of water sprays produced by the WL0.253 hydraulic nozzle in ambient temperature of different air flow environments at feed pressures (A) 3.5 bar, (B) 4.5 bar, and (C) 5.5 bars.

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# 5.4.2.2 Discussion of the water spray experiment results

The requirement for the spray freezing and freeze-drying to provide a narrow distribution is the key element for these nozzle selection experiments. The results form the PDA size measurements on the sprays exhibit a range of characteristics specific to the nozzles tested, the pneumatic nozzles produced finer, and faster sprays compared to the hydraulic nozzle, however the two pneumatic nozzles XA PR and SAM, displayed smaller variation in liquid atomisation characteristics. For all nozzles the atomisation pressure showed a distinct positive effect on the atomisation and spray distribution of these nozzles.

The atomisation produced by the pneumatic nozzle showed similar behaviour for equal ratios of atomisation gas to liquid feeds pressure. The arithmetic mean diameter,  $D_{10}$ , in the spray produced by the XA Pr050 nozzle at 1 bar gas and 1 bar liquid feed pressure, 10.58 µm, is similar to that of 2 bar gas and 2 bar liquid spray, 10.832 µm. This indicates that 1 bar atomisation gas is a sufficient atomisation gas feed for atomisation though the spray distribution would be enhanced by the increased pressure. A similar behaviour was noticed for the atomisation SAM nozzle. The latter had a constant atomisation performance at different pressures; this maybe due to the nozzle being an external mix type with a constant liquid feed design. Comparison of the relative span factor values for different pressures of each assembly indicates a better spray uniformity when both feeds are at equal pressure, which confirms the above finding. Therefore, it was proposed to operate the pneumatic nozzles with either, equal, or, higher atomisation gas to liquid feed pressures. The larger nozzle assemblies displayed a small increase of the drops mean sizes (5-15 %) and a large increase in velocities (40-50%) for both the XA and SAM nozzle. The large orifice assemblies, XA Pr100 and SAM 02-02, are not of a high interest for this research and, due to the large sizing on the spray drops, these assemblies (XA Pr100 and SAM 01-02) were no longer of interest in future spray testing measurement of the current research.

The spray produced by the SAM pneumatic nozzle at 1 bar gas and 2 bar liquid pressure was similar to that of the two other conditions tested, 1 bar gas + 1 bar liquid and 2 bar gas + 2 bar liquid, interpretation is that this nozzle has a lower atomisation gas requirement. This external mixing atomiser, SAM, produced slower mean velocity and wide DSD sprays compared to internal mix nozzle, XA Pr. The RSF figure that this nozzle, SAM, produces almost twice as much as the XA Pr nozzle spray, which is reflected in the broadness of the atomisation

distribution. Hence, considering all the above findings and the added complexity of the SAM nozzle set and operation, the XA Pr050 pneumatic nozzle was the preferred nozzle for continuing this line of research.

The second type of nozzle selected and examined in this research was the WL hydraulic nozzle which had a totally different atomisation mechanism. This is self evident by the results obtained from the PDA measurements. Due to the slow motion and, low momentum of this spray the effect of chamber environment on the spray characteristics was readily visible from the probability distribution function for the droplets in the spray. The droplet disintegration principle of the hydraulic nozzles is based on the momentum of the pressurised feed through a small orifice and the shears of the ligaments formed relative to the surrounding air to generate the individual drops. The characterisation results of this spray clearly display a different performance to that of the pneumatic nozzle.

The results shows that increasing the atomisation pressure resulted in an increase in the degree of atomisation, which is further aided by increasing the chamber gas flow. The spray seems to disintegrate more efficiently in the flowing environment and, the higher the surrounding gas velocity, the enhance break up or more drop disintegration above 4.5 bar atomisation pressures. The graphical representation of the spray distribution in figure (5-14) indicates an inter-relationship between the atomisation pressure and the flowing environment. The sprays produced in the flowing environment have a noticeable effect on the distribution, mostly in the 1.5 ms<sup>-1</sup> gaseous flow, whereas spraying into the 5 m/s flow produced an increase in the population of the droplets around the peak of the distribution. The high chamber gas flow rate was difficult to achieve and control, especially when operating in sub-ambient temperatures, and therefore this gaseous flowing environment was not used further.

The relative span factor for this hydraulic nozzle performance seems to confirm the better spray distribution in the flowing environment more than in stagnant air. This confirms the principle of drag enhancing liquid/drop disintegration. Though the flowing surrounding environment had no pattern of effect on the degree of atomisation produced by the pneumatic nozzle, this may be due to the higher disintegration caused by the atomisation gas that masks possible role of the surrounding gas. During the spray-freezing operation a constant flow of freezing medium is required to remove the heat input from the spray and maintain constant operating and chamber temperatures. Therefore, it proved better to plan the research for the

flowing environment since it is not altering the atomisation of the pneumatic nozzle and, yet aids the atomisation in the case of the hydraulic nozzle.

#### 5.4.2.3 Conclusions of the water spray experiments

The results can be summarised by and an understanding of the nozzle operations presented

- The XA series pneumatic nozzle has better atomisation performance in higher ratio of atomisation gas to atomised liquid feed pressures. The surrounding environmental flow has no apparent effect on the degree of liquid disintegration. The nozzle two different assemblies, Pr 050 and Pr 100, affect the degree of atomisation, but, over all, is mainly needed for increasing the mass flow of the liquid feed.
- The SAM series nozzle has a broader atomisation capacity than XA nozzle. It has comparatively better atomisation with equal liquid and gas feed and there for it is ideal for operation when low gas flow rate are required. The environmental chamber flow has no significant effect on the atomisation. The two assemblies available, S01-02, and S02-02, are affecting the atomisation flow capacity. Finally, the fanning operating assembly could not be used due to the excessive fogging of the chamber.
- The WL hydraulic nozzle has different performance criteria with a broad probability distribution function of size and requires an atomisation feed pressure above 4.5 bar for adequate performance. The surrounding environment plays a significant role in liquid disintegration.

In conclusion the pneumatic nozzles have a better spraying uniformity, in particular, the XA Pr050, due to its operational simplicity. The hydraulic nozzle, on the other hand, has the simplicity of a single feed medium through the nozzle but produce a characteristically coarse and low velocity spray. However, the current conclusions are for water sprays but the results may differ when spraying more viscous fluids. Thus, a second set of experiments were planned to test examine the effect of viscosity using the above findings to reduce the number of nozzles and tests.

#### 5.4.3 Spray characterisation of viscous liquids

The second series of experiments was intended to characterise the sprays produced by atomisation of liquid with different concentration of various materials suitable for use in spray-freeze-drying. The water sprays tested in the previous experiments have provided a
significant understanding of the performance of the available nozzle. The chosen nozzles were to be tested with more viscous liquids to examine the spray distribution at selected feed pressures. The aim was select an optimum operating pressure condition of the nozzles that is suitable for spray freeze-drying of water and concentrated liquids. The pressures were chosen such that the gas feed pressure was equal to, or, greater than the liquid feed pressure, in an attempt to find a combination which maximised the homogeneity of drop sizes.

## 5.4.3.1 Measurement strategy for viscous liquids

- Three nozzles were to used in this experiment the XAPr050 and SAM 01-02 pneumatic nozzles and the WL0.25 hydraulic nozzle.
- The organisation of the experiment is shown in figure (5-15) and listed in table (5-6).
- The spray operation was carried out at ambient temperature into flowing air at 1-1.5 ms<sup>-1</sup>.
- The sprays where measured at a distance of 60 mm below the nozzle orifice.
- The spray materials used were distilled water, sucrose concentrate (30%) and coffee concentrate (30%). Only one spray trial was performed for the coffee solution to investigate the PDA instrumental response when coffee concentrate was used.
- The water spray results were performed as a check for operational reproducibility with the results of preliminary experiment.

The temperature of the chamber environment was between 18-22 °C. The spray plume was relatively stable for a measurement time of 5-8 seconds before vision was inhibited due to fogging inside the chamber. The spray entrainment and turbulence of the sucrose concentrate spray created visual problems, in particular the build up of drops on the chamber windows. Build up on the laser inlet and light collection windows severely obstructed the PDA signal. The chamber was designed to enable swift removal of these windows for cleaning. Therefore, these glass windows were removed when contaminated for cleaning with water, and car glass polish, before the next test. One other problem encountered during chamber operations was the precise pressure setting of the atomising. The liquid feed pressurisation for the hydraulic nozzle could only achieve 5.0 bar pressure. Sucrose concentrate, due to the pressure drop across the pipe line with the high viscosity of the liquid. Therefore the initial test plan was altered, from 5.5 bar to 5.0 bar.

The operation of the XA pneumatic nozzle produced a back pressure in the liquid feed line resulting from the gas feed. This made the atomisation for the test (4 bar gas + 2 bar liquid) difficult as the gas feed inhibited the flow of the liquid feed. This lead to a policy of increasing the liquid feed pressure, making the test condition of (4 bar gas + 3 bar liquid).

Nozzle type	XA Pr50		SAM	WL 0.25	
Feed pressures	Liquid	Gas	Liquid	Gas	Liquid
Combination 1	1	1	1	1	3.5
Combination2	2	2	2	2	4.5
Combination3	3	2	3	2	5.5
Combination4	4	3	4	3	

Table 5-5: Plan of atomisation conditions for viscous spray characterisation experiment.



Figure 5-15: The spray organisation charts viscous spray characterisation experiment for the pneumatic and hydraulic spray nozzles.

## 5.4.3.2 Results

The summary of the data obtained for the different sprays at 60 mm below the spraying point are tabulated in tables (5-6) to (5-11). The drop size distributions are graphically illustrated in figures (5-16) to (5-22). The results, displayed by these normalised figures, indicate the following observations:

### XA Pr050 pneumatic nozzle

- The normalised water spray distribution shows a trend for a shift toward the small and narrow size distribution when increasing the atomisation pressure, up to 3 bar gas 2 bar liquid spraying condition, figure (5-16). At higher gas and liquid pressure the spray appears to lose atomisation quality.
- The sucrose spray distribution does not appear to follow the general trend above as the feed pressure increased, figure (5-17). The best sizing profile was achieved from the condition of 3-bar gas and 2 bar liquid test, similar to water spray, but with the difference that there is a reduction in the droplet population density of the spray.
- The spray appears to have similar drop size distributions when operating at the higher gas to liquid feeds pressure, figure (5-18). The 3 bar gas 2 bar liquid condition had the narrowest distribution even though a lower droplet population density is presented in the curve.

#### SAM 01-02 pneumatic nozzle

- The normalised water spray appears to have a consistent pattern in the drop size distribution, figure (5-19). The degree of atomisation is enhanced when spraying at the 1 bar gas 1 bar liquid condition, with reduced  $D_{10}$  and  $D_{32}$  values, while the peak drop count shifted to the small sizes of approximately 7µm.
- The sucrose concentrate spray distribution had a slight variation of size distribution with the feed pressure, figure (5-20). The distribution tend to increase in size with increasing atomisation pressures, and the best atomisation performance was achieved at 1 bar gas 1 bar liquid pressure.

### WL0.253 hydraulic nozzle

• The normalised water spray distribution appears consistent over the pressure range studied, figure (5-21).

• The sucrose concentrate spray distribution, figure (5-22), followed similar pattern but here the atomisation capability is reduced, with lower population density values.

**Table 5-6:** Summary data of water sprays produced by XA Pr050 nozzle in 1-1.5 ms<sup>-1</sup> flowingambient air environment.

XA pr050									
Atomisation set up and Experiment code	1 bar gas - 1 bar liquid <i>(XW11T1)</i>	2 bar gas - 2 bar liquid (XW22T1)	3 bar gas - 2 bar liquid (XW32T1)	4 bar gas - 3 bar liquid <i>(XW43T1)</i>					
Attempted Sample no.	203558	239038	239552	245628					
Validated Sample	181284	201854	202019	206662					
Data Rate (kHz)	101.778	125.094002	171.962997	142.893997					
Elapsed Time (Sec)	2.00	1.91	1.39	1.72					
U Vertical Velocity ms <sup>-1</sup>	42.78	55.48	82.75	101.71					
D <sub>10</sub> (μm)	12.54	13.19	8.56	11.69					
D <sub>20</sub> (μm)	14.20	14.54	9.28	12.41					
D <sub>30</sub> (μm)	16.04	16.12	10.00	13.30					
D <sub>31</sub> (μm)	18.15	17.83	10.81	14.18					
D <sub>32</sub> (μm) (SMD)	20.46	19.82	11.63	15.27					
D <sub>v0.5</sub> (μm) (VMD)	23.10	21.60	12.43	15.50					
D <sub>v0.9</sub> (μm)	40.89	40.04	19.04	25.67					
RSF	1,25	1.32	0.93	1.01					
D <sub>32</sub> /D <sub>10</sub>	1.63	1.50	1.36	1.31					
VMD/SMD	1.13	1.09	1.07	1.02					

Table 5-7: Summary data of sucrose concentrate 30% (w/w) sprays produced by XA Pr050nozzle in 1-1.5 ms<sup>-1</sup> flowing ambient air flowing environment.

XA pr050									
Atomisation set up and Experiment code	1 bar gas - 1 bar liquid <i>(XS11T1)</i>	2 bar gas - 2 bar liquid (XS22T1)	3 bar gas - 2 bar liquid (XS32T1)	4 bar gas - 3 bar liquid (XS43T1)					
Attempted Sample no.	122214	231217	231999	239504					
Validated Sample	114446	203456	201940	203779					
Data Rate (kHz)	61.11	164.14	157.84	173.60					
Elapsed Time (Sec)	2.00	1.41	1.47	1.38					
U Vertical Velocity ms <sup>-1</sup>	46.84	63.23	82.54	101.97					
D <sub>10</sub> (μm)	14.37	10.76	8.82	10.21					
D <sub>20</sub> (µm)	15.71	11.87	9.59	10.96					
D <sub>30</sub> (μm)	17.18	13.15	10.54	11.83					
D <sub>31</sub> (μm)	18.78	14.54	11.52	12.73					
D <sub>32</sub> (μm) (SMD)	20.54	16.15	12.71	13.78					
D <sub>V0.5</sub> (μm) (VMD)	22.39	17.32	13.41	14.34					
D <sub>V0.9</sub> (μm)	37.96	31.48	22.65	23.58					
RSF	1.13	1.25	1.11	1.03					
D <sub>32</sub> /D <sub>10</sub>	1.43	1.50	1.44	1.35					
VMD/SMD	1.09	1.07	1.06	1.04					



Figure 5-16: Normalised water spray distribution produced by the XA Pr050 pneumatic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).



Figure 5-17: Normalised sucrose concentrate spray distribution produced by the XA Pr050 pneumatic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).

 Table 5-8: Summary data of 30% coffee concentrate spray produced by the XA Pr 050 in ambient temperature.

	X	A pr050		
1.5 ms-1 gas flow/ 30% coffee concentrate	1 bar gas - 1 bar liquid (XC11T1)	2 bar gas - 2 bar liquid (XC22T1)	3 bar gas - 2 bar liquid (XC32T1)	4 bar gas - 3 bar liquid (XC43T1)
Attempted Sample no.	144825	261891	195740	260349
Validated Sample	113070	199383	158086	194679
Data Rate (kHz)	72.411797	130.563995	97.868301	130.173996
Elapsed Time (Sec)	2.00002	2.00585	2.00003	2
U Vertical Velocity ms <sup>-1</sup>	40.555	61.562	74.092	84.462
V Horizontal Velocity ms <sup>-1</sup>	-0.333	-0.603	-1.401	-1.5
D <sub>10</sub> (μm)	11.559	10.234	8.678	8.193
D <sub>20</sub> (µm)	14.153	12.541	10.72	10.202
D <sub>30</sub> (µm)	19.65	18.039	16.041	15.757
D <sub>31</sub> (μm)	25.621	23.95	21.809	21.852
D <sub>32</sub> (µm) (SMD)	37.879	37.327	35.917	37.587
D <sub>V0.5</sub> (µm) (VMD)	63.2091	174.7924	193.6403	187.2267
D <sub>V0.9</sub> (μm)	225.5695	229.2946	228.7752	224.2185
RSF	3.321	1.23	1.114	1.129
$D_{32}/D_{10}$	3.27701	3.64735	4.13886	4.58770
VMD/SMD	1.66871	4.68273	5.39133	4.98116
$D_{v_{0.9}}/D_{32}$	5.955001	6.142862	6.369552	5.965320



Figure 5-18: Normalised 30% coffee concentrate spray distribution produced by the XA Pr050 pneumatic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).

Table 5-9	: Summary	data	of	water	sprays	produced	by	SAM	01-02	nozzle	in	1-1.5	ms <sup>-1</sup>
	ambient f	lowir	ng ai	ir.									

	SAN	1 S01-02		
Atomisation set up and Experiment code	1 bar gas - 1 bar liquid <i>(SW11T1)</i>	2 bar gas - 2 bar liquid (SW22T1)	3 bar gas - 2 bar liquid (SW32T1)	4 bar gas - 2 bar liquid <i>(SW42T1)</i>
Attempted Sample no.	109527	159024	231762	234690
Validated Sample	98554	140194	201826	201974
Data Rate (kHz)	54.763	79.511	128.182	130.997
Elapsed Time (Sec)	2.00	2.00	1.81	1.79
U Vertical Velocity ms <sup>-1</sup>	31.94	43.34	54.71	59.84
D <sub>10</sub> (μm)	11.36	12.76	11.37	11.51
D <sub>20</sub> (μm)	14.63	15.89	13.64	13.67
D <sub>30</sub> (μm)	19.80	20.66	16.94	16.70
D <sub>31</sub> (μm)	26.15	26.28	20.67	20.12
D <sub>32</sub> (µm) (SMD)	36.27	34.89	26.11	24.94
D <sub>V0.5</sub> (μm) (VMD)	55.49	50.77	34.18	31.94
D <sub>V0.9</sub> (μm)	130.73	113.11	83.05	74.81
RSF	2.06	1.91	2.06	1.96
D <sub>32</sub> /D <sub>10</sub>	3.19	2.73	2.30	2.17
VMD/SMD	1.53	1.46	1.31	1.28

**Table 5-10:** Summary data of sucrose concentrate 30% (w/w) spray produced by SAM 01-02 nozzle in 1-1.5 ms<sup>-1</sup> ambient flowing air.

SAM S01-02									
Atomisation set up and Experiment code	1 bar gas - 1 bar liquid (SSIITI)	2 bar gas - 2 bar liquid <i>(SS22T1)</i>	3 bar gas - 2 bar liquid (SS32T1)	4 bar gas - 2 bar liquid (SS42T1)					
Attempted Sample no.	89357	158526	179257	234033					
Validated Sample	80256	140192	159914	202973					
Data Rate (kHz)	44.678	79.261	89.628	128.581					
Elapsed Time (Sec)	2.00	2.00	2.00	1.82					
U Vertical Velocity ms <sup>-1</sup>	29.78	42.79	52.42	59.08					
D <sub>10</sub> (μm)	11.22	11.38	12.43	11.10					
D <sub>20</sub> (μm)	14.67	14.26	14.77	13.15					
D <sub>30</sub> (μm)	20.31	18.86	18.14	16.13					
D <sub>31</sub> (μm)	27.32	24.28	21.92	19.45					
D <sub>32</sub> (µm) (SMD)	38.89	33.01	27.36	24.28					
D <sub>V0.5</sub> (μm) (VMD)	60.55	47.32	35.09	30.71					
D <sub>ν0.9</sub> (μm)	142.73	130.59	84.77	79.00					
RSF	2.07	2.45	2.03	2.19					
D <sub>32</sub> /D <sub>10</sub>	3.47	2.90	2.20	2.19					
VMD/SMD	1.56	1.43	1.28	1.26					



Figure 5-19: Normalised water spray distribution produced by the SAM 01-02 pneumatic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).





WL0.25								
Atomisation set up and		Water spray		30% :	30% sugar solution spray			
Experiment code	3.5 bar (WW35TI)	4.5 bar (WW45T1)	5.0 bar (WW50T1)	3.5 bar (WS35T1)	4.5 bar (WS45T1)	5.0 bar (WS50T1)		
Attempted Sample no.	30294	40227	46169	28117	40400	49448		
Validated Sample	22463	31559	37385	15218	24148	31098		
Data Rate (kHz)	0.505	0.670	0.769	0.469	0.673	0.824		
Elapsed Time (Sec)	60.00	60.00	60.00	60.01	60.00	60.00		
U Vertical Velocity ms <sup>-1</sup>	15.11	16.72	17.68	14.60	16.40	17.46		
D <sub>10</sub> (μm)	57.07	53.58	52.56	66.29	60.83	59.00		
D <sub>20</sub> (μm)	74.32	69.22	67.87	86.40	79.17	76.77		
D <sub>30</sub> (μm)	89.05	82.97	81.38	102.41	94.26	91.72		
D <sub>31</sub> (μm)	111.23	103.24	101.27	122.86	117.33	114.37		
D <sub>32</sub> (µm) (SMD)	127.83	119.20	117.02	143.60	133.60	130.95		
$\overline{D_{V0.5}(\mu m)}$ (VMD)	151.71	140.31	138.61	168.44	158.34	155.21		
$D_{v0.9}(\mu m)$	208.04	201.51	197.69	219.06	213.01	212.22		
RSF	0.81	0.88	0.88	0.73	0.79	0.75		
$D_{32}/D_{10}$	2.24	2.22	2.23	2.17	2.20	2.22		
VMD/SMD	1.19	1.18	1.18	1.17	1.19	1.19		

Table 5-11: Summary data of water and sucrose concentrate 30% sprays produced by WL0.25 hydraulic nozzle in 1-1.5 ms<sup>-1</sup> ambient flowing air.



Figure 5-21: Normalised water spray distribution produced by the WL0.25 hydraulic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).



**Figure 5-22:** Normalised sucrose concentrate spray distribution produced by the WL0.25 hydraulic nozzle in ambient flowing air (1-1.5 ms<sup>-1</sup>).



Figure 5-23: Reproducibility check of water sprays produced different experimental times by the XA Pr050 pneumatic nozzle in 1.5 m/s chamber air flow, measured at 60 mm below the spray nozzle.







Figure 5-25: Reproducibility check of water sprays produced different experimental times by the WL 0.25 hydraulic nozzle in 1.5 m/s chamber air flow, measured at 60 mm below the spray nozzle.



Figure 5-26: The spray distribution comparison of water against sucrose and coffee concentrates produced by XA Pr050 pneumatic nozzle at 3 bar gas 2 bar liquid atomisation pressures in ambient flowing gas.

### 5.4.3.3 Discussion

The PDA results obtained for the sprays produced by the nozzles showed the expected behaviour of the atomisation process, fine and narrow distribution sprays for the pneumatic and coarse and wide distribution spray for the hydraulic nozzles. The large number of experimented parameters studied and the measured quantities obtained, in particular for the XA Pr050 nozzle, make it difficult to analyse all data exhaustively. Therefore, interpretation in this experiment is oriented to compare the uniformity of the drop size distribution in the spray, which is the main aim of these experiments.

The comparison of the reproducibility plots presented in figures (5-23) to (5-25) indicates some variation under nominally identical conditions. This raises the question of the operation setup of the atomisation feeds pressure to all the nozzles, which is to be investigated in the next experiment.

For the pneumatic nozzle, SAM 01-02, experiments the best atomisation, i.e. highest droplet population distribution, and most uniform size distribution was obtained at the 1 bar gas + 1 bar liquid pressure condition. This confirms the fact that this nozzle is suitable for low gas consumption operations. The XA Pr050 spray nozzle on the other hand showed less consistency in the DSD, of fine spray. The best operating condition obtained was the 3 bar gas and 2 bar liquid pressure condition, however the atomisation flow capacity was reduced for a viscous liquids as it took a longer time for liquid to disintegrate. The spray distribution of the three liquid materials sprayed at 3 bar gas 2 bar liquid, figure (5-26), indicate a different distribution for the coffee concentrate in comparison to water and sucrose. This may be reasoned by the physical properties of sugar solution is closer to water than that of coffee, Chapter 4 section 4.3.6, table 4-2. However, one unknown mechanism is the absorption of laser light by the coffee concentrate as the droplet diameter increases. The hydraulic nozzle sprays produced the best conditions at the 5 bar feed pressure.

The overall drop size distribution results of the SAM nozzle indicated a good atomisation performance at low atomisation gas consumption, but there were concerns over the complication of the atomisation gas and liquid feed lines setup and operation. This nozzle had three gas line feeds that had to be operated, in order, from solenoid valves. The nozzle body physically large and it is difficult to fit a nozzle body heater, and in the same time prevented

from freezing. The e drop size distribution produced by the XA nozzle was finer and more uniform distribution, at least for water spray. For these reasons it was proposed to put the use of the SAM nozzle on hold in the follow up investigations of the current research.

In conclusion, the best pneumatic atomisation nozzle selected for the spray freeze-drying process was the XA Pr 050 nozzle operated at 3 bar gas + 2 bar liquid pressure. This was due to the good atomisation capacity and narrow size range produced as well as the speed and simplicity of the nozzle operation. The hydraulic nozzle was also selected as single medium atomiser produces different type of spray, wide drop size distribution range with slow spary mean velocity, which could be used for comparison of spray freezing modelling. The best condition chosen to be operated at is 5.0 bar liquid feed pressure.

## 5.5 Spray freezing characterisation and measurements

The experimental plan of the spray freezing measurements by PDA characterisation was a novel approach to spray freeze and sizing modelling. There are a few practical considerations of the spraying operation and the freezing heat transfer interaction that need to be reviewed in order obtain some understanding of spray freezing process. These concerns are:

- The lower chamber temperatures may affect the viscosity of the feeds if cooled sufficiently before atomisation is completed. There may thus be an effect of chamber temperature on the particle size distribution.
- 2) Freezing is a time dependent heat transfer process, influenced by the liquid physical properties that lead to phase change, by various possible routes depending on how the nucleation process proceeds. The droplets, phase change may hinder the PDA characterisation measurements, by switching the dominant laser scattering and detection mode from refraction for the liquid phase, to the reflection mode for the solid phase. The design of the spray freezing chamber allowed a series of measurements to be made at different heights below the spraying point while investigating the liquid disintegration and sizing of the droplets and comparing the data with the previous stages of measurement under the same conditions.
- 3) Finally, the rate of freezing is dependent on the temperature gradient between the heat transfer mediums, which may have a relative affect on the degree of atomisation and the hydrodynamics of the spray.

Therefore the aim of this experiment is to use the selected atomisation conditions from the previous section to; (i) examine the effect of chamber temperature on the drop size distribution and velocity, and, (ii) investigate the effect of the freezing temperatures on the atomisation by comparing the measured spray data at different heights. Experiments were preformed for both the XA Pr050 (pneumatic) and the WL 0.25 (hydraulic) nozzles using both stagnant and flowing chamber gas.

## 5.5.1 Apparatus and Materials

The spray measurement chamber and PDA system used in this experiment were described earlier in this chapter. The spray atomisers used in this test were the:

- XA Pr 050 pneumatic nozzle operated at 3 bar atomisation gas (nitrogen) from
  - pressurised cylinder, and 2 bar liquid feed pressure.

- WL 0.253 hydraulic nozzle operated at 5.0 bars pressure generated from a pressure vessel filled with liquid and compressed air.
- The feed liquid was distilled water.
- The freezing medium used in the spray freezing operations was LN<sub>2</sub>, vaporised into N<sub>2</sub> gas at (-62 °C, -42 °C, and -22 °C ± 2 °C).
- The drop size distributions were Results were compared, in all cases, to the ambient tests performed at 20°C.

The experimental examination of the spray freezing measurements was carried out in four separate sessions. An organisational plan for these experimental sessions, and dates of testing, are shown in figure (5-27).

The first experimental session aimed to measure the spray under three varying parameters

- Four temperatures, 20 °C, -22 °C, -42 °C, & -62 °C all  $\pm 2$  °C.
- These sprays were measured at two heights, 60 & 160 mm below the spray nozzle.
- All spray freezing tests were carried out for both flowing & non-flowing chamber gas.

The second experiment session was performed to confirm the findings of the first spray freezing in a flowing environment measurement at 160 mm below the spray nozzle, and to provide a reproducibility measure of the first session. Die to the spreading of spray cone down stream the detected population in the centre of the cone is lowered. Therefore drop population density testing is not of interest in this research, as much as the shape of the spray distribution and absolute velocity of the drops.

The third experimental session was carried out to measure the spray characteristics mapped at four different locations down stream of the spraying point, to investigate the change and progress of the atomisation between the ambient and one selected chamber temperature. The results obtained in the first spray freezing measurements had defined the best operation temperature and the gaseous environment conditions for this spray freezing experiment, i.e. the no-flow gas (stagnant) and a temperature of  $(-42 \pm 2)^{\circ}$ C. The measurement height started from 60 mm below the spray nozzle of the XA Pr 050 pneumatic nozzle and was measured at further three down stream locations of 100, 160, and 220 mm of the spray nozzle.

The fourth experimental session was carried to repeat the spray measurements conditions for the third experimental session on a different type of spray, atomisation of liquid feed by the WL 0.25 hydraulic nozzle, which have different pattern of drops dynamics in the freezing zone. Therefore, this test experiment is designated to measure water sprays in two temperatures conditions at four different location beneath the nozzle.

# 5.5.1.1 Problems in applying PDA to the analysis of freezing spray

There were a few problems encountered during the PDA spray characterisation study at subambient temperatures; e.g. nozzle blockage due to feed freezing, external humid air leaks into the system causing fogging, spray turbulence inside the chamber causing additional fogging and mixing, reduced accuracy in the pressure settings of the atomised feed pressures and spray pulsation. These problems were assessed individually, based on the experimental observation, and solved separately without affecting the over all process performance; and they were listed in Chapter 3 section 3.1.10.

The problem of fogging in the chamber, and hence, the presence of multiple fog droplets in the PDA measurement volume, could be monitored by the PDA "gain/drop size estimate", which is sensitive to optical clarity inside the chamber. All measurements were commenced only when an acceptable level of clarity was reached indicated by a "gain/drop size estimate" of  $D_{10}$  value below 5µm. The laser power and photo detector voltages were also increased for sub-ambient PDA measurements to reduce the attenuation of the beam due to fogging. The swirling fog also lead to instability in the measurement volume that lead to a spatial oscillation of the measurement point. Hence the PDA measurement setting configuration was changed, from 2 components to a 1 component velocity measurement only.

In the first few tests of this experiment the atomisation pressure set-up was subject to a thorough check on the reproducibility of the pressure setting and the subsequent DSD. These test trials were performed by varying the atomisation gas pressure setting, by a needle width either side of the 3 bar graduation on the pressure dial gauge. The results exhibited a clear variation in the drop size distribution when comparing the  $D_{10}$ ,  $D_{32}$ , and  $D_{v0.9}$  and graphical distributions. Hence the spraying operation feed line was modified, by employing an electronic transducers, for accurate operational setting and enhancing the reproducibility of the tests. This produced acceptable results as seen later.

First Session





Fourth session



Figure 5- 27: Organisation plan of the experiments.

### 5.5.2 Results

The results obtained from all the measurement are presented relative to the type of nozzle and starting with the summary of the test as planned in the day. Summary data for these sprays are tabulated and graphically presented by normalised drop size distribution charts separately. The mean velocity of these spray populations is also profiled to exhibit the variation in velocity for the drop size counts in each class of the distribution by a standard deviation ( $\pm$  STDV). The velocity results are thus first discussed here, along with size information discernable from the tabulated data.

In the third experimental session investigating the pneumatic nozzle a measurement attempt was carried at only 30 mm below the spray nozzle. The measurement was not possible as the spray was very fast, with some velocities higher than the velocity measurement bandwidth of the PDA system instrument. Further more, the liquid feed appeared to be still within the ligament disintegration zone as the sample count per second of the spherical drops was not significant. Therefore, 60 mm below the spray nozzle was identified as a good first point of measurement for the liquid disintegration from the pneumatic nozzle.

To enable comparisons to be made more easily of the effect of different conditions the results of all experimental sessions are presented in multiple plots of the following

The XA pneumatic nozzle;

- Spray data at the same temperature and flow condition at different measurement heights.
- Spray data at the same measurement height and flow condition but at different temperatures.
- Spray data at the same temperature and measurement height but different flow conditions.

The WL hydraulic nozzle;

- Spray data at the same temperature at different measurement heights.
- Spray data at the same measurement height and different temperatures.

These plots are accompanied by a discussion of the drop size distributions, DSD.

## 5.5.2.1 First spray freezing characterisation

Table 5-12: Summary data of water spray in a variable temperatures and flowing gaseous environment produced by XA Pr050 pneumatic nozzle at 3bar  $N_2$  atomisation gas feed and 2 bar water liquid feeds, measured at two different points below the nozzle orifice.

XA Pr050 (3 bar gas & 2 bar liquid feed pressures)								
	28301	28302	28303	28304	28305	28306	28307	
Measurement point (mm)	60	60	60	60	60	60	60	
Temperature °C	$20 \pm 2$	$(-22 \pm 2)$	$(-22 \pm 2)$	$(-42 \pm 2)$	$(-42 \pm 2)$	$(-62 \pm 2)$	$(-62 \pm 2)$	
Freezing gas (m/s)	00	0	1.5	0	1.5	0	1.5	
Attempted Sample no.	243801	285435	271134	99196	325527	310009	182261	
Validated Sample	205587	213043	216555	82366	221493	218871	114873	
Data Rate (kHz)	196.281	58.9020	58.5882	19.8391	83.2459	112.717	36.4503	
Elapsed Time (Sec)	1.24	1.80	4.63	5.00	3.91	2.75	5.00	
U Vertical Velocity ms <sup>-1</sup>	105.265	111.504	114.581	114.251	109.865	109.045	103.443	
$\mathbf{D}_{10}(\mu \mathbf{m})$	9.957	10.436	11.705	12.445	11.545	11.284	11.733	
D <sub>20</sub> (μm)	10.601	11.099	12.391	13.233	12.316	12.044	12.675	
D <sub>30</sub> (μm)	11.275	11.733	13.063	14.231	13.047	12.775	13.771	
D <sub>31</sub> (μm)	11.998	12.441	13.801	15.217	13.870	13.593	14.919	
D <sub>32</sub> (μm) (SMD)	12.756	13.112	14.521	16.457	14.641	14.371	16.254	
D <sub>V0.5</sub> (μm) (VMD)	13.242	13.567	14.913	16.293	15.164	14.875	16.447	
D <sub>V0.9</sub> (μm)	19.820	19.779	21.893	30.876	22.207	21.933	30.148	
RSF	0.852	0.788	0.787	1.222	0.794	0.807	1.187	
$D_{32}/D_{10}$	1.281	1.256	1.241	1.322	1.268	1.274	1.385	
$D_{V0.9}/D_{32}$	1.554	1.508	1.508	1.876	1.517	1.526	1.855	

XA Pr050 (3 bar gas & 2 bar liquid feed pressures)								
	28308	28309	28310	28311	28312	28313	28314	
Measurement point (mm)	160	160	160	160	160	160	160	
Temperature °C	$20 \pm 2$	$(-22 \pm 2)$	$(-22 \pm 2)$	$(-42 \pm 2)$	$(-42 \pm 2)$	$(-62 \pm 2)$	$(-62 \pm 2)$	
Freezing gas (m/s)	0	0	1.5	0	1.5	0	1.5	
Attempted Sample no.	83336	20270	8052	38516	22601	33091	52784	
Validated Sample	82603	16024	5488	28205	15252	22388	35982	
Data Rate (kHz)	16.6658	4.05292	1.60919	7.70288	4.51854	6.61806	10.5563	
Elapsed Time (Sec)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	
U Vertical Velocity ms <sup>·1</sup>	28.89	24.73	22.14	23.74	22.07	22.20	26.45	
D <sub>10</sub> (μm)	12.83	12.27	12.38	11.14	11.74	11.43	17.84	
D <sub>20</sub> (μm)	13.63	14.49	15.32	13.50	14.42	13.94	21.76	
D <sub>30</sub> (μm)	14.47	18.29	20.61	17.68	19.40	18.14	26.26	
D <sub>31</sub> (μm)	15.37	22.32	26.61	22.28	24.94	22.87	31.86	
D <sub>32</sub> (µm) (SMD)	16.32	29.11	37.33	30.33	35.11	30.72	38.22	
D <sub>V0.5</sub> (μm) (VMD)	17.25	31.13	46.01	36.61	43.66	35.05	40.03	
D <sub>V0.9</sub> (μm)	25.38	228.36	211.78	215.93	225.28	231.33	210.47	
RSF	0.84	6.88	4.25	5.52	4.81	6.19	4.70	
$D_{32}/D_{10}$	1.27	2.37	3.02	2.72	2.99	2.69	2.14	
$D_{V0.9}/D_{32}$	1.55	7.84	5.67	7.12	6.42	7.53	5.51	



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Figure 5-28: Water Spray by XA Pr 050 pneumatic nozzle measured at 60 mm below the spray nozzle. Graph on the (left) are normalised spray distributions per total attempted samples for each test. Graphs on the (right) represents the mean velocity profiles of the drops in the spray tested, with an error bar showing  $\pm 1$  STDV.

The results displayed in figure (5-28) and table (5-12) indicate the following:

- The mean drop size of the spray (DSD) increases when lowering the temperature of the freezing gas surrounding the spray.
- II) The velocities of the spray droplets are all of a similar magnitude to each other with the standard deviation of approximately 20% of the mean. This is despite the large range in terminal velocities for the different drops. This very much suggests that the spray moves as a cloud with only small relative motion between different drops
- III) The mean velocity of the sprays indicates at this point of measurement the large droplets have a higher velocity profile than the smaller ones. Each profile has a similar elongated "S" profile with a plateaux at the high and low sizes. The mean velocity values of the sprays are reduced with temperature. The error bars of the standard deviation values of these velocities are similar for most drops in the spray range, but are slightly higher for large drops, which are more than likely be due to their low number count.
- IV) The effect of the flow environment on the atomisation in the freezing condition has not presented in any noticeable effect on the spray.



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Figure 5-29: Water spray produced by XA Pr 050 at 3 bar gas 2 bar liquid, and measured 160 mm below the spraying point. The graphs on the (left) are the normalised spray distribution per the total attempted sample of each test. The graphs on the (right) represent the mean drop velocities of the sprays, with an error bars representing  $\pm 1$  STDV.

The results of spray measured at 160 mm beneath the spraying point are presented in figure (5-29) and indicate the following:

- The (DSD) of the spray appears to shift toward the smaller drop sizes indicating a possible secondary disintegration at lower temperatures compared to that of ambient spray.
- II) The mean velocity profile for the size range of the spray drops seems to even out to form a uniform velocity profile at this location of the chamber, having decelerated from  $(100 \pm 20)$ m/s at 60 mm to  $(20\pm10)$  m/s at 160 mm. Though the ambient temperature spray velocity profile still shows an "S" shape, this is less marked in the sub-ambient gas environment.
- III) Similarly, as with the measurement at the 60 mm location there is no obvious effect of the gas flow that can be reported from the graphical representation. However, the table analysis indicates smaller values of  $(D_{32}/D_{10})$  for the sprays produced in a non-flowing gaseous environment.
- IV) The final results of the spray produced in a flowing freezing gas  $(-62 \pm 2)^{\circ}$ C indicated an abnormality in size distribution and velocity of the produced spray in addition to the results of the D<sub>32</sub> value obtained in point III. All the results showed smaller drop counts comparing to that obtained at 60 mm height.

# 5.5.2.2 Second Spray freezing characterisation

 Table 5-13: Summary data of water sprays produced by the XA Pr050 pneumatic nozzle in flowing gas at different temperatures, measured 160 mm below the nozzle.

XA Pr050 (3 bar gas & 2 bar liquid feed pressures)								
	3405	3406	3407	3407 (Repeat)	3408			
Measurement point (mm)	160	160	160	161	160			
Temperature °C	$20 \pm 2$	$(-22 \pm 2)$	$(-42 \pm 2)$	$(-42 \pm 2)$	$(-62 \pm 2)$			
Freezing gas (m/s)	No flow	Flow	Flow	Flow	Flow			
Attempted Sample no.	103810	46631	19429	23362	20842			
Validated Sample	102643	36694	13588	16382	13949			
Data Rate (kHz)	20.7619	9.32295	3.8849	4.67076	4.16831			
Elapsed Time (Sec)	5.00	5.00	5.00	5.00	5.00			
U Vertical Velocity ms <sup>-1</sup>	28.291	24.989	23.761	24.065	21.749			
D <sub>10</sub> (μm)	11.126	11.626	12.786	12.296	12.291			
D <sub>20</sub> (µm)	11.949	13.975	16.364	15.316	15.273			
D <sub>30</sub> (µm)	12.831	18.522	24.711	21.938	21.250			
D <sub>31</sub> (µm)	13.778	23.379	34.353	29.303	27.941			
D <sub>32</sub> (µm) (SMD)	14.795	32.537	56.347	45.007	41.133			
D <sub>V0.5</sub> (µm) (VMD)	15.773	38.399	213.244	190.282	69.817			
D <sub>V0.9</sub> (µm)	23.842	221.785	230.062	226.600	225.718			
RSF	0.913	5.400	0.984	1.099	2.989			
$D_{32}/D_{10}$	1.330	2.799	4.407	3.660	3.347			
$D_{y_0} q/D_{z_2}$	1.611	6.816	4.083	5.035	5,488			







Figure 5-30: Water spray produced by XA Pr 050 at 3 bar gas 2 bar liquid feed pressures, and measured 160 mm below the spraying point, repeated test. The graphs on the (left) are the normalised spray distribution per the total attempted sample of each test. The graphs on the (right) represent the mean drop velocities of the sprays, with error bars showing ±1 STDV.

The results obtained in table (5-13) indicate a lower count of drops measured in this experiment compared to the similar conditions of the previous experiment, but, the graphical analysis of this spray drop size distributions and mean velocity profiles are consistent with the previous experiment's findings.

### 5.5.2.3 Third spray freezing characterisation

**Table 5-14:** Summary data of water sprays produced by the XA Pr050 pneumatic nozzle in non-flowing gas environment at different temperatures, measured for different heights (60, 100, 160, and 220 mm) below the nozzle orifice.

XA pr050 (3 bar gas and 2 bar liquid feed pressures)							
	12501	12502	12503	12504			
Measurement point (mm)	60	100	160	220			
Temperature °C	20 ± 2	$20 \pm 2$	20 ± 2	$20 \pm 2$			
Freezing gas (m/s)	No flow	No flow	No flow	No flow			
Attempted Sample no.	216898	209213	58547	18272			
Validated Sample	203176	201195	57922	18180			
Data Rate (kHz)	144.35	66.645302	11.7082	3.65429			
Elapsed Time (Sec)	1.50	3.14	5.00	5.00			
U Vertical Velocity ms <sup>-1</sup>	83.098	46.420	25.435	17.267			
D <sub>10</sub> (μm)	11.399	11.650	12.519	13.580			
D <sub>20</sub> (μm)	11.986	12.558	13.485	14.525			
D <sub>30</sub> (μm)	12.604	13.433	14.481	15.574			
D <sub>31</sub> (μm)	13.196	14.424	15.574	16.678			
D <sub>32</sub> (µm) (SMD)	13.817	15.368	16.699	17.903			
D <sub>V0.5</sub> (μm) (VMD)	14.322	16.440	17.875	18.493			
D <sub>V0.9</sub> (μm)	20.294	23.259	26.516	32.032			
RSF	0.742	0.784	0.872	1.101			
$D_{32}/D_{10}$	1.212	1.319	1.334	1.318			
D <sub>V0.9</sub> /D <sub>32</sub>	1.469	1.513	1.588	1.789			

XA pr050 (3 bar gas and 2 bar liquid feed pressures)							
	12505	12506	12507	12508	12509	12510	
Measurement point (mm)	60	100	160	220	160	220	
Temperature °C	$(-42 \pm 2)$						
Freezing gas (m/s)	No flow						
Attempted Sample no.	253294	25117	3482	5048	36566	8646	
Validated Sample	217630	19182	2473	3334	25851	5785	
Data Rate (kHz)	92.2435	5.02239	0.69617	1.0095	7.31306	1.72902	
Elapsed Time (Sec)	2.75	5.00	5.00	5.00	5.00	5.00	
U Vertical Velocity ms <sup>-1</sup>	79.052	39.151	21.366	13.417	20.113	13.26	
D <sub>10</sub> (μm)	12.507	13.855	13.123	11.58	11.047	11.456	
D <sub>20</sub> (μm)	13.287	15.918	15.773	15.645	14.148	15.583	
D <sub>30</sub> (μm)	14.022	18.663	18.602	24.574	21.096	24.808	
D <sub>31</sub> (μm)	14.846	21.661	22.148	35.798	29.153	36.506	
D <sub>32</sub> (µm) (SMD)	15.615	25.656	25.874	60.631	46.901	62.876	
D <sub>V0.5</sub> (μm) (VMD)	16.1266	26.2358	31.5858	221.2651	175.6856	195.9546	
D <sub>V0.9</sub> (μm)	23.0465	186.0739	53.081	224.9943	225.3249	229.4465	
RSF	0.746	6.534	1.218	0.919	1.184	1.058	
$D_{32}/D_{10}$	1.24850	1.85175	1.97165	5.23584	4.24559	5.48848	
D <sub>V0.9</sub> /D <sub>32</sub>	1.475921	7.252647	2.051519	3.710879	4.804266	3.649190	



Figure 5-31: Water spray produced by XA Pr 050 pneumatic nozzle at 3 bar gas 2 bar liquid sprayed in ambient air measured at different heights. The graphs on the (left) are the normalised distribution per attempted samples measured in the spray. The graphs on the (right) are the mean velocity profile of the sprays, with error bars showing ±1 STDV.



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Figure 5-32: Water spray produced by XA Pr 050 pneumatic nozzle at 3 bar gas 2 bar liquid sprayed in freezing gas at  $(-42 \pm 2)$  °C, measured at different heights. The graphs on the (left) are the normalised distribution per attempted samples measured in the spray. The graphs on the (right) are the mean velocity profile of the sprays, with error bars showing ±1 STDV.

The results summarised and in table (5-14) and figures (5-31) and (5-32) display expected trends based on the previous experiments of spray broadening and reduction in the velocity profiling of the spray down stream the from the nozzle. These results can be best viewed when compared with previous results in a single chart, (see figure(5-39)).

## 5.5.2.4 Fourth spray freezing characterisation

Table 5-15: Summary data of water sprays produced by the WL 0.253 hydraulic nozzle in non-flowing gas environment at two different temperatures, measured at different heights (38, 68, 108, 168, and 228 mm) below the nozzle orifice.

WL0.25 Hydraulic nozzle (5 bar feed pressure)							
	5601	5602	5603	5604	5605		
Measurement point (mm)	228	168	108	68	38		
Temperature °C	$(20 \pm 2)$						
Freezing gas (m/s)	No flow						
Attempted Sample no.	5000	5931	9665	20729	46272		
Validated Sample	4668	5538	8842	18026	31354		
Data Rate (kHz)	0.24998	0.29651	0.48316	1.03644	2.3136		
Elapsed Time (Sec)	20.00	20.00	20.00	20.00	20.00		
U Vertical Velocity ms <sup>-1</sup>	10.233	11.725	14.860	16.798	19.140		
$D_{10}(\mu m)$	50.405	51.802	53.188	43.564	49.826		
$D_{20}(\mu m)$	64.777	66.431	67.759	57.928	62.853		
D <sub>30</sub> (μm)	77.822	79.448	80.874	70.791	74.241		
D <sub>31</sub> (μm)	96.699	98.390	99.726	90.240	90.623		
$D_{32}(\mu m)(SMD)$	112.323	113.932	115.211	105.720	103.581		
$D_{V0.5} (\mu m) (V M D)$	138.962	134.628	136.648	125.221	119.380		
$D_{V0.9}(\mu m)$	197.256	197.437	199.105	189.478	185.994		
RSF	0.936	0.942	0.916	0.971	1.000		
$D_{32}/D_{10}$	2.228	2.199	2.166	2.427	2.079		
$D_{V0.9}/D_{32}$	1.756	1.733	1.728	1.792	1.796		

WL0.25 Hydraulic nozzle (5 bar feed pressure)							
	5606a	5606b	5607a	5607b	5608a	5608b	
Measurement point (mm)	38	38	68	68	108	108	
Temperature °C	$(-42 \pm 2)$						
Freezing gas (m/s)	No flow						
Attempted Sample no.	4736	3056	1344	1616	704	688	
Validated Sample	2664	1872	1141	1393	602	615	
Data Rate (kHz)	1.32323	0.85948	0.52277	0.45054	0.21179	0.17915	
Elapsed Time (Sec)	3.57913	3.55562	2.5709	3.58673	3.32401	3.84026	
U Vertical Velocity ms <sup>-1</sup>	19.836	20.295	18.49	18.02	16.758	17.323	
D <sub>10</sub> (μm)	61.27	66.558	59.244	56.459	69.054	68.481	
<b>D</b> <sub>20</sub> (μm)	71.418	77.135	69.265	67.182	80.704	80.255	
D <sub>30</sub> (μm)	81.175	87.031	78.834	77.315	92.152	91.061	
D <sub>31</sub> (μm)	93.434	99.52	90.938	90.475	106.453	105.005	
D <sub>32</sub> (μm) (SMD)	104.868	110.795	102.119	102.395	120.148	117.232	
D <sub>V0.5</sub> (μm) (VMD)	119.2413	126.5054	118.6033	116.3944	137.2077	137.2845	
D <sub>V0.9</sub> (μm)	205.7939	195.3543	180.0381	173.8801	208.5882	199.4625	
RSF	1.174	0.986	0.984	0.938	0.971	0.904	
$D_{32}/D_{10}$	1.71157	1.66464	1.72370	1.81362	1.73991	1.71189	
$D_{V0.9}/D_{32}$	1.962409	1.763205	1.763023	1.698131	1.736094	1.701434	



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Figure 5-33: Water spray produced by WL 0.25 hydraulic nozzle at 5 bar feeds pressure in ambient air measured at different heights. Graphs on the left show normalised distributions per total attempted sample number of each spray test. Graphs on the right are the mean velocity profile of each test, with error bars showing ±1 STDV.



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Figure 5-34: Water spray produced by WL 0.25 hydraulic nozzle at 5 bar feeds pressure at a chamber gas temperatures of  $-42 \pm 2$  °C measured at different heights. Graphs on the left normalised distribution per total attempted sample number of each spray test. Graphs on the right are the mean velocity profile of each test, with error bars showing  $\pm 1$  STDV.

The sprays produced by the hydraulic nozzle have relatively small velocity values at the atomisation pressure of 5 bar, which enables accurate measurement of the spray at shorter distances than 60 mm below the spray nozzle. Hence the operational conditions for the measurement were; water sprayed at 5 bar into ambient and sub-ambient temperatures,  $(-42 \pm 2)^{\circ}$ C, and a non-flowing gas environment measurement at five locations down stream the nozzle (38, 68, 108, 168, and 228 mm). These results presented a different spray pattern to the freezing effect on the atomisation and spray hydrodynamics. The key features can be summarised as follows:

- The measured spray count reduces with increased distance from the nozzle. This reduced even further with low temperature spray conditions. These measurements repeating at some locations and abandoning measurements at greater than 108 mm distance.
- II) The normalised drop size distribution plots, figure (5-33), indicate a pattern at ambient temperatures that shows different characteristics from the freezing operations, figure (5-34), changing the PDF profile from "half Gaussian" into a "skewed Gaussian" shaped curve with higher count variation between class sizes.
- III) The mean velocity profiles of the spray drop population at ambient temperatures, figure (5-33) shows plateaux of a "tick mark" shape, where the larger drops have higher velocities. These sprays decelerate with distance travelled downstream the relative variation between the drop velocities with size. This variation tend to maintaining equal drop velocities across the size range with their descend. In the sub-ambient conditions,

figure (5-34), this behaviour is not so well displayed as the drop count for the sprays was small.

## 5.5.2.4.1 Comparative pneumatic water spray distribution plots









Figure 5-36: Normalised distribution of water spray produced by XA Pr050 in stagnant gaseous environment at different temperatures measured 100 mm below the spraying point.



Figure 5-37: Normalised distribution of water spray produced by XA Pr050 in stagnant gaseous environment at different temperatures measured 160 mm below the spraying point.



Figure 5-38: Normalised distribution of water spray produced by XA Pr050 in stagnant gaseous environment at different temperature measured 220 mm below the spraying point.



## Equal temperature and flow conditions as a function of measurement location

Figure 5-39: Normalised distribution of water spray produced by XA Pr050 in ambient stagnant gaseous environment measured at different heights below the spraying point.



Figure 5-40: Normalised distribution of water spray produced by XA Pr050 in sub-ambient temperature stagnant gaseous environment (-22 ± 2)°C measured at different heights below the spraying point.



Figure 5-41: Normalised distribution of water spray produced by XA Pr050 in sub-ambient stagnant gaseous environment  $(-42 \pm 2)^{\circ}$ C measured at different heights below the spraying point



Figure 5-42: Normalised distribution of water spray produced by XA Pr050 in sub-ambient stagnant gaseous environment  $(-62 \pm 2)^{\circ}$ C measured at different heights below the spraying point



## Equal height and temperature as a function of flow conditions

Figure 5-43: Normalised spray distribution comparison of water spray at ambient and subambient temperatures (-22 ± 2)°C produced by XA Pr050 Pneumatic nozzle in different gas environment measured at 60 mm below the spraying point



Figure 5-44: Normalised spray distribution comparison of water spray at ambient and subambient temperatures (-42 ± 2)°C produced by XA Pr050 Pneumatic nozzle in different gas environment measured at 60 mm below the spraying point.



Figure 5-45: Normalised spray distribution comparison of water spray at ambient and freezing temperatures (-62 ± 2)°C produced by XA Pr050 Pneumatic nozzle in different gas environment measured at 60 mm below the spraying point.



Figure 5-46: Normalised spray distribution comparison of water spray at ambient and subambient temperatures (-22 ± 2)°C produced by XA Pr050 Pneumatic nozzle in different gas environment in different gas environment measured at 160 mm below the spraying point.



Figure 5-47: Normalised spray distribution comparison of water spray at ambient and subambient  $(-42 \pm 2)^{\circ}$ C temperatures produced by XA Pr050 Pneumatic nozzle in different gas environment measured at 160 mm below the spraying point.



Figure 5-48: Normalised spray distribution comparison of water spray at ambient and subambient temperatures  $(-62 \pm 2)^{\circ}$ C produced by XA Pr050 Pneumatic nozzle in different gas environment measured at 160 mm below the spraying point.

### 5.5.3 Discussion of the spray freezing experiments

The particulate size control of the spray freeze-drying process proposed by a follow up operations of spraying, freezing, and freeze-drying. The produced particles have a size distribution, which is dependent on the spray nozzle type and atomisation pressures. But the earlier freezing spray characterisation of the PDA had shown an influence of the chamber gas on liquid disintegration that was not investigated previously. The atomised liquid will be solidified into a particulate when released into freezing medium, however, the need to achieve total solidification before particle collisions and wall interactions occur are a concern, also for spray drying operations. This practical problem is fundamental in determining the SFD process efficiency and quality performance, it must be considered both theoretically and experimentally. PDA spray characterisation is a tool for the assessment of spray size and hydrodynamic performance that can be used to minimise, or eliminate, the risk of drop to wall interaction and agglomeration of drops prior to freezing by aiding mathematical modelling of the freezing and drying process.

The spray drops decelerate due to drag of the surrounding gaseous environment and undergo a thermally induced phase transition from a liquid to a solid state. The gas contacting the drops form a surrounding interface, the "boundary layer", through which heat transfer and, mass transfer if any, takes place. This layer is mathematically defined by the region of velocities whose magnitudes was less than those for a potential flow due to the retarding effect of friction on shear at the interface (Ranz *et al.* 1952). The latent heat of freezing is transferred across this boundary layer from the droplet to the gas stream. The extent of spray freezing depends on the freezing rate governing mechanisms and the residence time within the spray freezing zone. This is dictated by both the drop velocity and the its relative slip velocity. The heat transfer coefficient (h) is determined from the physical properties of the cooling medium, i.e. viscosity, density, thermal conductivity, specific heat capacity at constant pressure, and flow velocity, and the boundary layer dimensions, as well as the characteristic dimensions of the flow channel.

The droplet velocity and size data collected from the spray freezing experiment allows a new vision of the liquid disintegration mechanism, especially when analysing the operation with the simultaneous heat transfer process. There are a number of observations made from theses data that can be used to modify the physical on modelling of the heat transfer during the

spraying operation in general, and spray freezing in particular. The best approach to this analogy is to consider the spray velocity distribution separate from the droplet population frequency distribution.

#### 5.5.3.1 Spray velocity profile

Two different characteristic patterns of the spray velocity profiles were obtained from nozzles used in these experiments. The drop mean velocity of a spray appears to a have arrange across the drop size distribution range, also it is variable within the class size of the spray DSD.

#### 5.5.3.1.1 Velocity profile of the pneumatic sprays

The pneumatic nozzle produces a high velocity spray, 90-130 m/s, with high values for standard deviation STDV, 40 %, for each size class of the spray. The velocity profiles presented in figures (5-25) and (5-26) initially are "S" shaped, with the larger drops having higher velocities, i.e. momentum, while the smaller drops have lower velocities which are presumably, similar to that of the entrained gas. The profile curvature is flattened as the drop descending down stream until the drops approaches the terminal velocities relative to the moving gas stream at the point. In addition, the overall spray cloud tends to decelerate with distance down stream the nozzle. However, this occurred earlier in the sub-ambient experiments as the velocity profile of the spray straightened at the 100 mm position in comparison to that of ambient operations. It is possible to explain this by the higher drag caused by the denser sub-ambient gas. It is also clear when comparing the curvature of the initial plots from the measurements at the 60 mm location for the ambient and sub-ambient operations. The comparison of the first, with the third, experiments may indicate a difference in the velocity profile but this may be due to the experimental errors in setting of the atomisation feeds pressure and temperature and/or the gas flow regulation of the operational set up, i.e. operational inconsistencies between experiments.

#### 5.5.3.1.2 Velocity profile of the hydraulic sprays

The second type of spray velocity profile was produced by the hydraulic nozzle. These data have a smaller velocity 10-25 m/s, in comparison to the pneumatic nozzle one, which is expected. The STDV range of the drops in each class is approximately 40 to 50 %. The plateaux like profile shape at 38 mm of figure (5-27) is categorised by three regions of size classes:

- i) Size class  $0-10 \,\mu$ m, shows higher velocities than the rest of the spray.
- ii) Size class 10-25 µm, uniform velocity (first plateaux).
- iii) Size class >25 μm, which shows a gradual increase in velocities with measurement location height, until a second plateaux is reached.

The velocity profile of the spray measurement in a descending locations shows an expansion of the first size class plateaux to higher sizes, this can be interoperated by one of two possibilities; (a) increasing the population of the first plateaux due to possible drops disintegration, or (b) the drops are approaching their terminal velocity relative to the gas stream of the measured location, which is more likely.

In the freezing spray measurements, the spray produced by the hydraulic nozzle varied distinctly from the ambient spray, the results shows an increase in the range of the first class size region to include the fully disintegrated drops in the class size 0-10  $\mu$ m, starting from the first measurement location. This class size tend to disappear from the velocity profile as descending in the measurement location heights, which indicates (a) possible freezing of the drops, or, (b) an increase in measurement error of the small drops due to a lowering of a light transmission. The final region of the largest drops maintained a similar trend as that of the ambient operation and become the dominant velocity profile measured in the spray at greater distances.

The overall velocity profile of the spray decelerates with height, which is an expected feature since the spray cloud gradually slows. No significant difference can be noticed in the velocity values between the ambient and sub-ambient measurements.

## 5.5.3.2 Spray size distribution

The decision to analyse the drop size distribution using the normalised distribution per total attempted samples was based on the concern of the spray characterisation of liquid materials under going a phase change. The drops will have different scattering responses to the laser beam and hence the velocity/size estimates may not provide a complete picture. An object passing through the measurement volume, i.e. the fringe pattern, generates both refracted and or reflective signals, the proportion will depend on the drops phase state. The object will trigger a measurement to be attempted in the optical sensor but the signal may be rejected for particle size and velocity determination. According to the setup of the PDA instrument in this

experiment only the refracted light signals were accepted, which is typical case of liquid drops. If the presence of a solid phase interferes with the scattered refracted light beyond a certain extent the data will be rejected and thus give an incomplete picture of the spray. Hence, it can be postulated that an increase in the rejection rate can be related directly be due to drop freezing. If the distributions are normalised against total attempted samples and compared against ambient distributions, then, the rejected samples in each size interval, for the sub-ambient condition, can be readily observed by the differences between the normalised population frequencies.

# 5.5.3.2.1 The spray size distribution (DSD) of the pneumatic nozzle

The normalised size distributions of the sprays measured under different temperature conditions and distances from the pneumatic nozzle are shown in figures (5-35) through to (5-48).

The general observation of the freezing spray size distribution shows an increase in the population of the small drops, this may be due to PDA instrument pretence producing a size readings of the drops smaller than what they are, or, these drops are a results of a large disintegrations, which is a scenario that is not proven yet. These are tentative hypothesis presumed but not confirmed without further investigations. Other interesting observation is what described as "limiting distribution", which is the drop size distribution of the spray is limited to certain range at a specific height and temperature.

The results provide on overall picture of the measurement reproducibility and the effect of varying the chamber operational conditions on the spray, these results described as follows:

# Effect of temperature on the spray DSD (figures (5-35) to (5-38)):

At 60 mm below the nozzle only a mild change in the size distribution is seen with changing temperature. The DSD decreases in area, i.e. a lower drop count, and shifts to a slightly larger size distribution. As the distances from the nozzle increases the DSD markedly decreases in area, the overall rejection rate increases, which may be attributed to drop freezing, but there is an increase in the number of smaller drops (<5  $\mu$ m). The sprays at the -22 °C temperature condition has a distribution close to that of ambient temperature than the other freezing at this

conditions, especially with the heat capacity from the atomisation pressure gas and flow introduced in the chamber.

There appears to be a "limiting distribution", e.g. that for 160 mm and -62 °C, figure (5-37), which is similar for a number of experimental combinations of temperature and height below which the DSD does not appear to change, in term peak area nor breadth.

# Effect of measurement at heights on the spray DSD (figures (5-39) to (5-42)):

The size/velocity data at descending distances display further disintegration of the spray indicated by reduction in the peak height of the drop size distribution for the sprays. Also peak area tend to show an increase in the small drop population. This has a possible mean of the drops were further disintegrated to a finer drops in the distance between the initial height and the measured next height. The figures (5-40) to (5-42) show an increase in the counts of drops between 1-4  $\mu$ m at freezing temperature over that for ambient spray of the same location. The curves in figures (5-39) and (5-40) reflects the scenario of increasing the population density of the larger drop sizes down stream from the measurement point of 60 mm, in all temperature conditions. It could be postulated that there is the possibility of droplet collision and integration from the small sizes producing larger agglomerates, or in the freezing conditions the possible delay in disintegration of the liquid.

# Effect of flow conditions on spray DSD (figures (5-43) to (5-48)):

There are same variations between the DSDs for flowing and non-flowing chamber gas conditions, however, these are of the same order of magnitude for differences between nominally identical runs. No significant differences can therefore be drawn from these data and we can assume that chamber flow conditions have no effect on the near nozzle spray development.

# General thought and conclusion

The reproducibility check of the results obtained shown in plots of figures (5-39) to (5-42), demonstrate a high level of consistency in the size distribution pattern for the matching test repeats, but there is still a small degree of variation in the drop density populations DSD's for nominally identical sprays. This variation can be restrained considering the operational inconsistencies between experiments and the effect of the external environment on the spray

operation and measurement in particular during freezing conditions. The results presented in the figures (5-40) to (5-42) indicated that the freezing temperature of  $-42 \pm 2^{\circ}C$  for the stagnant flow had a reasonable atomisation capability and a reproducible result, which lead to the conclusion of adopting this temperature to be the ideal testing operation for mapping the spray at different down stream locations for both the pneumatic and the hydraulic nozzles.

The results also show a delay in disintegration during freezing operation presented by the increase in small drop population at lower heights. This complies with the Marshall's (1954) statement that increasing in the viscosity will lead to a delay in the disintegration process, for pressurised sprays (Marshall 1954).

## 5.5.3.2.2 The spray size distribution (DSD) of the hydraulic nozzle

This nozzle produced a spray with a wide size distribution generated by shear forcing the liquid feed by pressurising through an orifice. The drag forces of the surrounding environment plays a significant in the disintegration process than that of pneumatic nozzle, as proved in experiment 1. The normalised distributions of the sprays measured at different temperatures and distance from the nozzle are shown in figures (5-49) through to (5-53).



## Different height same temperature sprays

Figure 5-49: Normalised distribution of water spray at ambient temperatures produced by WL 0.253 hydraulic nozzle at 5 bar atomisation pressure in a non-flowing gaseous space measured at different heights below the spraying point.



**Figure 5-50:** Normalised distribution of water spray in a sub-ambient gas  $(-42 \pm 2)^{\circ}$ C produced by WL 0.253 hydraulic nozzle at 5 bar atomisation pressure measured at different heights below the spraying point.



## Different temperature same height sprays

Figure 5-51: Normalised spray distribution comparison of water spray at ambient and subambient temperatures produced by WL 0.253 hydraulic nozzle at 5 bar atomisation pressure measured at 38 mm heights below the spraying point.



Figure 5-52: Normalised spray distribution comparison of water spray at ambient and subambient temperatures produced by WL 0.253 hydraulic nozzle at 5 bar atomisation pressure measured at 68 mm heights below the spraying point.



Figure 5-53: Normalised spray distribution comparison of water spray at ambient and subambient temperatures produced by WL 0.253 hydraulic nozzle at 5 bar atomisation pressure measured at 108 mm heights below the spraying point.

## Effect of measurement at heights on the spray DSD (figures (5-49) to (5-50)):

The comparison of the DSDs for the water sprays at ambient temperature and at different heights, figure (5-49) indicates that at 38 mm the spray is still disintegrating, as the population increases for the 68 mm measurements; thereafter, the spray has a reasonably consistent population count. At sub-ambient conditions the sprays have a different pattern of spray distribution, figure (5-50), and the assessment of individual size distribution curves indicates a possible case of increasing the liquid resistance to the disintegration process since the frequency plots oscillates wider across the class size distribution when compared with the ambient temperature operations.

# Effect of temperature on the spray DSD (figures (5-51) to (5-53)):

A comparison of ambient and sub-ambient sprays indicates that the continuous disintegration at 38 mm for both conditions suggest a reduction in the population count of the drops in the range of 1-20  $\mu$ m that could be due to either, an agglomeration of the viscous drops, which is highly unlikely, or a delay in the disintegration of the drops compared to ambient. Alternatively they may have been rejected for sizing estimates as they were partially frozen. This might also be expected to occur preferentially in the smaller drop size classes which have a higher surface area to volume ratio and therefore freezes first.

The overall understanding of these results of the spray measurement in a comparative study for the freezing and ambient operations can be listed to the following possibilities

- Agglomeration of the spray drops leads to increasing in the drop sizing down stream the chamber. It is unlikely scenario in the ambient spraying operations, but its is a possible scenario for the freezing sprays.
- The decrease in the operational temperatures increases the liquid viscosities and possibly leads to affecting the drop size, and delaying the spray disintegration at sub-ambient conditions down stream from the nozzle.
- The velocity profiles for the pneumatic spray are changeable across the drop size range and they tend to stabilise when the drops loose their momentum of the atomisation gas and reach the relative velocity gradually.
- The velocities of the drops in the sprays produced by the hydraulic nozzle are decelerating studiously progressed with descending height until the terminal velocity relative to the gas, once they are fully developed drops.

The results of the sprays measured in this research were used to model the spray freezing operation and establishing a real time prediction of the freezing time of water in the designed rig for this research.

## 5.6 Spray freezing modelling

Spray freezing is a complex process involving, heat transfer, fluid dynamics and crystallisation. The particle gas slip velocity affects the rate of heat transfer which in turn governs the drop temperature and hence the crystallisation kinetics.

The spray is a two-phase flow consists of a continuous gaseous phase and a discrete droplet phase. Droplet size, freezing gas temperature, and ice nucleation temperature are major parameters in this operation influencing the process of heat transfer and the rate of freezing (Liao *et al.* 1990; Masters 1991; Gao *et al.* 2000; Hindmarsh *et al.* 2003). The specification for the design of a spray freezing chamber requires the complete freezing of the particles. A freezing model to be used in the design thus needs to predict the freezing profile of phase change within the object. The phase change profiling of drop freezing is an important interest in spray freezing operations to accommodate the prediction of particle freezing in a designated operation time (especially of the largest particles) prior to contact to the chamber wall.

The objective of this modelling section is to examine the validity of PDA spray freezing characterisation measurements. The spray freezing model study in this chapter was subdivided into stages;

- Developing a freezing model for falling single drop using the Pham (1984) model in conjunction with the Hindmarsh (2003) model.
- (ii) Applying the model to predict freezing time of drops in a spray using 3 different methods of estimating the particle gas slip velocity, assuming a constant gas temperature.
- (iii) Analyse the PDA velocity results to estimate the time taken for drops to reach different distances from the nozzle. This will allow the comparison of freezing times predicted from the above model to those observed in the PDA experiments.

## 5.6.1 Single drop freezing model

#### 5.6.1.1 Falling droplet dynamics

Droplet freezing involves a number of features, but these all derive from the particle slip velocity. It is thus important to be able to quantify this. The drop released from the spray

nozzle into a spraying chamber has a relatively higher speed than the gas circulating inside the chamber, though its velocity dissipates with time rapidly due to gas friction The droplet movement in the spray-freezing chamber goes through three stages

- 1. Droplet formation after release from the nozzle.
- 2. Droplet deceleration in the spraying chamber due to the drag of the chamber gas.
- 3. Steady motion with the gas/velocity slip velocity close to the terminal velocity.

The study of the droplet-gas flow field requires number of assumption to ease the prediction of the flow field.

- The freezing gas is an ideal gas.
- The freezing gas density and thermo-physical properties are constant.
- The droplet density and thermo physical properties are dependent on phase change only.
- The droplets are perfect spheres.
- The droplet diameter is constant

The drop/particle travels through the spray chamber in a motion affected by the forces acting on its body such as gravity, drag, and buoyancy. The object properties such as size, shape and density affect these forces and motion. The relative motion of the droplet or particle in the flowing environment causes the drag force which is the most influential force. This opposes the direction of motion and defined as

$$F_{D} = \frac{A_{p}C_{D}\rho_{g}v_{p}^{2}}{2}$$
 Eq (5-10)

Where  $F_D$ 

= the drag force (N) = the drag coefficient (dimensionless)  $C_D$ 

= projected area in the direction of motion, for a sphere =  $\pi r^2$  (m<sup>2</sup>).  $A_p$ 

= droplet relative velocity (m/s)  $v_p$ 

= fluid density  $(kg/m^3)$  $\rho_g$ 

= fluid viscosity (Pa.s)  $\mu_g$ 

There are a number of empirical formulas to calculate the drag coefficient of gas particle flows derived by different researchers for trajectory calculations in various applications. White (1974) proposed a single particle drag formula valid over a wide range of Reynolds number (Kladas et al. 1993), which is reasonably useful for spray-freezing modelling due to it simplicity.

$$C_D = 0.4 + \frac{24}{\text{Re}} + \frac{6}{1 + \sqrt{\text{Re}}} \text{ Re (0 to 2x10^5)}$$
 Eq (5-11)

The value of the slip Reynolds (Re) number is determined from knowing the droplet diameter, velocity in relation to the gas, and the physical properties of the gas (density and viscosity),

In the SFD process the droplets are released from the nozzle into a cold gaseous stream, which subsequently undergoes phase change process due to freezing, the consider the solidification of the droplet (spherical) occurs on the surface first and thence advances to the centre, so the surface of the droplet is hardened almost instantaneous. The trajectory and moment properties of the drops usually studied in term of its relative velocity to the moving stream. The absolute velocity of the drop usually determined either mathematically from the formulation of the exit velocity when the mass flow rate of the liquid atomised and the cross section area ( $A_n$ ) of the nozzle.

The weight less the buoyancy force is given by

$$F_{g} = \frac{\pi}{6} D_{p}^{3} (\rho_{p} - \rho_{g}) g$$
 Eq (5-13)

Where  $\rho_p$  = droplet or a particle density (kg/m<sup>3</sup>). g = acceleration due to gravity 9.81 m/s<sup>2</sup>.

Thus the overall force on the droplet is given by  $F_g - F_D$ . At terminal velocity the net force is zero. Thence the droplets settling under gravity force and have low Reynolds number (Stokes Law). Hence, the terminal velocity is, assuming the droplet is totally frozen when it reaches the terminal velocity  $(v_l)$  so

$$v_{t} = \frac{D_{p}^{2}g(\rho_{p} - \rho_{g})}{18\mu_{g}}$$
 Eq (5-14)

This uses a different expression for a  $C_D$  from equation (5-11). The droplet/particle density depends on its phase state. For a two phase droplet which is transforming from liquid to solid the density can be estimated from

Where (*x*) is the solid fraction. Droplet deceleration value is calculated according to Newton's  $2^{nd}$  Law, net force = mass\* deceleration.

$$\alpha = \frac{dv_p}{dt} = -\left(\frac{\rho_g C_D A_p v_p^2}{2m}\right) + \frac{\pi}{6m} D_p^3 (\rho_p - \rho_g) g \qquad \text{Eq (5-16)}$$

Where m = is the droplet mass (kg)A = is drop deceleration (m<sup>2</sup>)

This equation can also be used with some confidence for the case of a single drop falling in a steady gas flow. It is used for a drop released from a spray nozzle with a small spraying cone angle, predominantly moving in a vertical plane and can be considered as a one-dimensional motion in a gravitational field. However, the determination of the  $(v_p)$  is difficult and will be variable in turbulent flows.

Spray freezing of this research is a limited operation by the amount of the liquid feed, up to 250g, sprayed at atmospheric pressure in a sub-ambient  $N_2$  gaseous environment (-25 to -65 °C). Theoretically, the proposed freezing operation is rapid within the confined cylindrical area of the spraying chamber. The current model will consider a droplet subjected to *convective heat transfer only*. Any evaporative or sublimative cooling is assumed to be negligible due to the short residence time.

The relative velocity and the droplet movement in the spray-freezing chamber prescribe the heat transfer coefficient that is determined from a dimensionless Nusselt number. There are different formulation of this dimensionless number, but the one adopted in this spray freezing model is that used in the spray drying modelling (Ranz *et al.* 1952; Masters 1991), what is known as Ranz and Marshall equation.

$$Nu = 2 + 0.6 \,\mathrm{Re}^{0.5} \,\mathrm{Pr}^{0.33} \qquad \qquad \mathrm{Eq} \ (5-17)$$

The estimation of the heat transfer coefficient over a range of slip velocities of 0-100 m/s in  $N_2$  gas at -45 °C was calculated from equation (5-17) and presented graphically in figure (5-54). The graph shows existing effect of slip velocity on heat transfer coefficient. There is a factor of 4 variation in heat transfer coefficient between slip velocity of 0 and 100 m/s. The heat transfer coefficient is only a weak function of slip velocity. However, a certain percentage error in estimating slip velocity will translate into a much smaller percentage error in estimating the heat transfer coefficient.



**Figure 5- 54:** The relation between the heat transfer coefficient and slip velocity of a 20 μm drop in sub-ambient nitrogen gas at -45 °C.



Figure 5- 55: Terminal velocity of water spray DSD in ambient and sub-ambient freezing gas.

## 5.6.1.2 Freezing of falling droplet model

Models for freezing were briefly reviewed in Chapter 2. In this research it has been decided to adopt the Pham (1984) model whilst adding a recalescence stage used by Hindmarsh (2003). The complete freezing process is sub-divided into

- Cooling period, the material temperature drops down below the freezing point temperature to a nucleation temperature.
- Recalescence period, where rapid crystal growth occurs at the expense of sensible heat. Here the droplet temperature rapidly raised to the freezing point temperature accompanied by conversion of liquid water to solid ice.
- A slower phase change period occurs at the freezing mean temperature of the material, for water (0 °C), until solidification is complete.
- Finally the sub-cooling period, here the material temperature continues to drop down until it reaches the storage freezing temperature.

The supercooling period described as duration of the liquid continues cooling below the freezing temperature without crystallisation occurring. Eventually a nucleation temperature  $(T_n)$  is reached, its value dependent on the nature and amount of nucleator present in the drop (Liao *et al.* 1990; Hindmarsh *et al.* 2003). In most calculations were used as a value of (-5 °C). At this point recalescence occurs where by crystal growth takes place at the expense of sensible heat in the droplet until the droplet had risen to the freezing temperature.

For a spherical droplet moving in a vertical plane of a constant spray with time in liaison with Pham model described in Chapter 2, section 2.4.4.1, the heat of freezing diffuses from the droplet centre to the surrounding gas forming a boundary layer convected into the gas stream, then freezing time determined from the summing time of the above stages.



Pham assumed in his model that the Biot number (Bi) is constant through each stage including that of the phase change stage.

Where

$$Bi = \frac{hD}{k_0}$$
 Eq (5-18)

$$k_2 = (\Delta F \times k_1) + ((1 - \Delta F) \times k_{ice})$$
 Eq (5-19)

For a 20  $\mu$ m drop moving at a velocity of 10 m/s the Biot no. is 0.15 (W/mK) reduced to 0.04(W/mK) when the drop reaches its terminal velocity. This means that for a freezing drop the role of Biot no. on the freezing heat transfer is minimal. The Hindmarsh model essentially assumed Biot number of zero.

Freezing of the droplet is considered in the form of temperature changes of the liquid to that of the freezing mean temperature  $(T_f)$  of the material at  $\Delta t$  time step. By integrating equations (2-23 to 25) from Chapter 2 section 2.4.4.1, the freezing profile of the drop is predicted in response to heat transfer to the gas. For the first stage the temperature change  $(\Delta T)$  in a time interval  $(\Delta t)$  is found from the following relation

$$\Delta T = \frac{\Delta t A h (T - T_a)}{m C_l \left(1 + \frac{B i_1}{6}\right)}$$
 Eq (5-20)

See Chapter 2, section 2.4.4.1 for the nomenclature.

When the droplet temperature is the nucleation temperature  $(T_n)$ . The freezing stage begins (phase change). In this freezing period the parameter of interest is the fraction of the solidified liquid within the droplet  $\Delta F$ , which is calculated from deriving equation 6 while the temperature remains constant ( $T = T_f = T_c$ ).

$$\Delta F = \frac{\Delta t A h (T - T_a)}{m \lambda \left(1 + \frac{B i_2}{4}\right)}$$
 Eq (5-21)

The tempering or sub-freezing cooling stage begins after when all freeze-able` water in the drop is solidified, i.e.  $\Delta F = 1$  and the  $T_c$  is equal to  $T_f$ . Thence, the final freezing temperature of the droplet determined by equation (5-22), sub cooling stage, using in this equation the specific heat capacity value of ice when calculating the Biot number.

$$\Delta T = \frac{\Delta t A h (T - T_a)}{m C_{ice} \left(1 + \frac{B i_3}{6}\right)}$$
 Eq (5-22)

Here the sub-freezing tempering stage would end at the time where the droplet centre reaches final temperature of storage value ( $T_{fi}$ ). Pham had established this model in order to derive more accurate and simplified equation to predict the overall freezing time of a matter. In his assumptions he lacked the information of the heat transfer resistance Biot number with time

during the freezing operation. Though in the current modified spray freezing model this parameter was approximated as a function of the phase change with time which allows reasonable of the freezing front profiling.

#### 5.6.2 Freezing time estimation of a falling drop at various slip velocities

In a preliminary simulation the above model was applied to determine the freezing time of a single water drop (20  $\mu$ m) in a still sub-ambient nitrogen gas (-25, -45, and -65 °C) at particle gas slip velocities regimes

- i) At its own terminal velocity (0.015 m/s),
- ii) Fixed velocity of (10 m/s), and
- iii) Decelerating droplet with initial relative velocity of 90.64 m/s (as measured by PDA) according to the model described in the previous section. Here it is the droplet relative velocity rather than the absolute velocity that is of interest, so uncertainties in the gas velocity are of limited importance.

The decelerating drop was also applied to simulate the freezing time to selected sizes of water sprays produced by a pneumatic and hydraulic nozzles in an attempt to evaluate the spray freezing operation performance. The mean velocity data from the PDA measurements at 60 mm below the nozzle were used as the initial drop velocity when released from the nozzle. The simulation was preformed to sprays produced in -25, -45, and -65 °C sub-ambient gas environment, using the initial velocity of that measured at -45 °C.

The PDA measurement had detected a range of drop sizes and velocities of the water sprays that decelerate in a characteristic pattern to the nozzle type, in both ambient and sub-ambient temperatures. The usual practice for heat and mass transfer modelling of sprays is to use an average mean diameter such as  $D_{32}$ ,  $D_{V0.5}$ , and  $D_{V0.9}$ , and spray mean velocity to establish the operational time (Gauvin *et al.* 1976; Masters 1991). The PDA measurement provided these diameters, but the mean velocity was of the overall spray drops. Therefore, four drop size diameters representing fine, mean, median, and large drops in the spray size distribution where chosen to be used in the spray freezing model to provide a picture of the freezing time profile of the spray. For the XA Pr050 pneumatic nozzle the chosen drop sizes were 2, 5, 10, and 20  $\mu$ m, and for the WL 0.25 hydraulic nozzle sprays the sizes were 20, 50, 100, and 150  $\mu$ m.

### 5.6.2.1 Results and discussion

The estimated freezing temperature vs. time profiles shown in figure (5-56) indicate that a 20  $\mu$ m drop will freeze in 14 milli-seconds, depending on the relative velocity profiling of the drop. The drop travelling at fixed slip velocity equal to terminal velocity has almost twice long freezing time than that travelling with 10 m/s velocity. This indicates an effect of the drop relative velocity on the freezing profile due to the consequence variation in the heat transfer coefficient. The simulation of freezing time of a droplet travelling in variable relative velocity had a medium range of solidification time (approximately 10.5 milli second), which confirms the role of the flowing gas surrounding the drop on the rate of heat transfer by the effect of the drag. Perhaps the most striking feature, however, is that even large differences in velocity profiles still result in freezing times of the same order of magnitude.

In the second simulation part the simulation freezing time profile results were presented graphically in figure (5-57) and (5-58). For the sprays produced at -45 °C the changes in heat transfer of the decelerating drop was also presented for each drop sizes in figures (5-59) and (5-60).







**Figure 5- 57:** Simulated freezing time profile of a selected water drop sizes in a spray produced by the XA Pr050 pneumatic nozzle. (A) spray at -25 °C . (B) spray at -45 °C and (C) spray at -65 °C.







Figure 5- 59: Simulation of the heat transfer coefficient value change with time (left) and droplet velocity profile against distance (right) for decelerating drops of water spray produced by XA Pr050 pneumatic nozzle in a sub-ambient nitrogen gas at -45 °C.



**Figure 5- 60:** Simulation of heat transfer coefficient value change with time (left) and droplet velocity profile against distance (right) for decelerating drops of water spray produced by WL 0.25 hydraulic nozzle a sub-ambient nitrogen gas at -45 °C.

In this sheet the time (in seconds) required for a drop to reach first the nucleation temperature  $(T_n)$  and second the complete solidification during freezing was estimated. This estimation was carried for rang of drop sizes (2, 5, 10, 20, 50, 100, and 150 µm), freezing gas temperatures, and nucleation temperatures, using modified Pham (1984) freezing model. The tables shown the time estimated for a drop travelling at its own terminal velocity (table C-i), and at 10 m/s slip velocity in Table (C-ii). Four nucleation temperatures were proposed for this estimation (-5, -10, -15, and -20 °C) repeated in three different freezing gas temperatures (-25, -45, and -65 °C).

<b>Fable</b>	5-	16:	Time	fro	drops	in	spray	to	reach	$T_n$	and	complete	freezing	(F	=	I)	while
			travel	ling	at it te	rmi	nal ve	loci	ity, sus	pen	ded.						

				Varial	ble $v_t$				
2 micron		Time (sec	) taken to re	ach Tn			Time (sec)	taken to rea	ich F = 1
T <sub>en</sub> /	$T_{g}$	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.00004	0.00003	0.00002		-5	0.00024	0.00015	0.00011
	-10	0.00006	0.00003	0.00003		-10	0.00025	0.00015	0.00011
	-15	0.00008	0.00004	0.00003		-15	0.00026	0.00015	0.00011
	-20	0.00012	0.00006	0.00004		-20	0.00029	0.00016	0.00012
5 micron									
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.00031	0.0002	0.00016		-5	0.0015	0.00092	0.0007
	-10	0.00043	0.00026	0.0002		-10	0.00155	0.00092	0.00071
	-15	0.00059	0.00032	0.00024		-15	0.00163	0.00092	0.00071
	-20	0.00086	0.0004	0.00029		-20	0.00182	0.00092	0.00073
10 micror	1								
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	Tg	-25	-45	-65
	-5	0.00127	0.00098	0.00277		-5	0.00598	0.00365	0.00277
	-10	0.00173	0.00127	0.00279		-10	0.00613	0.00369	0.00279
	-15	0.00236	0.00173	0.00282		-15	0.00644	0.00376	0.00282
	-20	0.00345	0.00236	0.00287		-20	0.00722	0.00388	0.00287
20 micror	1								
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.00498	0.00321	0.00249		-5	0.02332	0.01417	0.01071
	-10	0.00675	0.00409	0.00312		-10	0.02385	0.01431	0.01079
	-15	0.00924	0.00511	0.0038		-15	0.02511	0.01459	0.01091
	-20	0.0135	0.00632	0.00456		-20	0.02814	0.01506	0.01112
50 micror	1	1.1							
T <sub>en</sub> /	$T_{g}$	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.02782	0.0177	0.01356		-5	0.07809	0.05819	0.05819
	-10	0.03769	0.02257	0.01695		-10	0.07888	0.05857	0.05857
	-15	0.05161	0.02819	0.02066		-15	0.08042	0.05926	0.05926
	-20	0.07537	0.03484	0.02476		-20	0.08299	0.06035	0.06035
100 micro	on								
T <sub>en</sub> /	$T_{g}$	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.08824	0.05494	0.04107		-5	0.4133	0.2427	0.17646
	-10	0.11954	0.07006	0.05134		-10	0.41918	0.24154	0.1776
	-15	0.16365	0.08751	0.06258		-15	0.41918	0.2499	0.1797
	-20	0.20959	0.10815	0.07501		-20	0.41918	0.25786	0.18296
150 micro	n								
T <sub>en</sub> /	$\mathbf{T}_{\mathbf{g}}$	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.15676	0.096	0.07044		-5	0.73576	0.42488	0.30328
	-10	0.2124	0.1224	0.08804		-10	0.75228	0.42912	0.30516
	-15	0.29076	0.15292	0.10732		-15	0.7916	0.43736	0.30872
	-20	0.42468	0.18896	0.12864		-20	0.83836	0.45124	0.31428

Table	5-	17:	Time	fro	drops	in	spray	to	reach	$T_n$	and	complete	freezing	(F	=	l)	while
			travel	ling	at 10 r	n/s	slip ve	eloc	city.								

				v = 10	m/s				
2 micron		Time (sec	) taken to re	ach Tn			Time (sec)	taken to rea	ch F = 1
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	$T_{g}$	-25	-45	-65
	-5	0.00009	0.00002	0.00001		-5	0.00022	0.00011	0.00008
	-10	0.00004	0.00002	0.00002		-10	0.00018	0.0001	0.00008
	-15	0.00006	0.00003	0.00002		-15	0.00019	0.00011	0.00008
	-20	0.00009	0.00004	0.00003		-20	0.00022	0.00012	0.00009
5 micron									
T /	т	.25	-45	-65	т /	т	-25	-45	-65
Len /	-5	0.0002	0.00012	0.00009	Len /	-5	0.00097	0.00057	0.00042
	-10	0.00027	0.00012	0.00012		-10	0.00099	0.00058	0.00043
	-15	0.00027	0.00010	0.00012		-15	0.00104	0.0006	0.00043
	-20	0.00055	0.00025	0.00017		-20	0.00117	0.00062	0.00044
10 .									
T. /	і Т.	-25	-45	-65	T /	T.	-25	-45	-65
ren /	-5	0.00072	0.00045	0.00033	ren /	-5	0.00341	0.00201	0.00146
	-10	0.00097	0.00057	0.00033		-10	0.00348	0.00202	0.00146
	-15	0.00133	0.00071	0.00051		-15	0.00366	0.00206	0.00149
	-20	0.00195	0.00088	0.00061		-20	0.0041	0.00213	0.00151
	20	0100170	0100000	0100001		20	0.0011	0100210	0100101
20 micror	ı								·
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	Tg	-25	-45	-65
	-5	0.00245	0.00152	0.00113		-5	0.01155	0.00675	0.00489
	-10	0.00332	0.00194	0.00141		-10	0.01181	0.00682	0.00492
	-15	0.00455	0.00242	0.00172		-15	0.01242	0.00695	0.00497
	-20	0.00665	0.00299	0.00207		-20	0.01391	0.00717	0.00507
50 micror	1	÷							
T <sub>en</sub> /	$T_{g}$	-25	-45	-65	T <sub>en</sub> /	Tg	-25	-45	-65
	-5	0.01182	0.00726	0.00535		-5	0.0557	0.03227	0.02316
	-10	0.01601	0.00926	0.00669		-10	0.05694	0.03258	0.0233
	-15	0.02192	0.01156	0.00816		-15	0.05989	0.0332	0.02356
	-20	0.03201	0.01429	0.00978		-20	0.06703	0.03424	0.02397
100 micro	n								
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	$T_g$	-25	-45	-65
	-5	0.03765	0.023	0.01686		-5	0.17801	0.10251	0.0731
	-10	0.05102	0.02933	0.02108		-10	0.1819	0.10347	0.07351
	-15	0.06984	0.03663	0.02569		-15	0.19126	0.10541	0.07433
	-20	0.102	0.04527	0.03079		-20	0.20959	0.10868	0.07564
150 micro	n								
T <sub>en</sub> /	Tg	-25	-45	-65	T <sub>en</sub> /	Tg	-25	-45	-65
	-5	0.07343	0.04471	0.03268		-5	0.34792	0.19974	0.14196
	-10	0.09948	0.05701	0.04084		-10	0.35544	0.20157	0.14275
	-15	0.13619	0.07121	0.04979		-15	0.37362	0.2053	0.14431
	-20	0.1989	0.08801	0.05967		-20	0.41788	0.20959	0.14682

The simulation shows that droplet freezing time according to this model is inversely proportional to drop size and velocity, that is typical of heat transfer operation relationships between drops size and gases. The heat transfer coefficients plots in figures (5-59) and (5-60) shows a reduction in the heat transfer coefficient with time while the droplet decelerating, until it reaches a steady level at the terminal slip velocity. This indicates the rate of heat transfer is higher during decelerates descend of the drop and it is different than that of a drop travelling in a fixed slip velocity. It was established in section 5.5 that the drop population in a spray moves in a cloud pattern and the gas of drops in of the same size have a range of velocities. If this range of range correspond to the gas droplet slip velocity, it is then varies in a proportional factor with descending distance for the drop. The graph in figure (5-55) shows a limited effect of the slip velocity on the heat transfer coefficient of the freezing, and in turn freezing heat transfer rate.

The spraying feed inputs into the freezing environment will have a significant role on the rate of heat transfer as there is a heat transfer from the liquid feed warming up the surrounding gas (at least at the boundary layer), and in the case of the pneumatic spray the atomisation gas input will play a role in diluting the gas temperature in the spray cloud. The consequence of this issue will raise a question about the practicality of the steady gas freezing gas temperature during the spray freezing modelling. The rigorous answer measure the gas temperature at multiple points along a vertical axis in a centre of the spray providing temperature distance profile to be introduced into the operation and incorporating the data into the freezing model.

Here the question will be raised is a single drop freezing model an adequate predictor freezing time of spray knowing that the drops in a spray moving in a cloud, as reported by the PDA measurement in section 5.5.

#### 5.6.3 PDA result evaluation through the spray freezing model

The velocity of the sprays measured by the PDA was carried at some distance below the spray nozzle, as the spray disintegrates at a distance from the nozzle orifice, before which fully developed drops have a higher velocity which is not measured. This section was designated to estimate the drop initial velocity in a spray uses the measured mean velocity data of the selected drop sizes from both the hydraulic and pneumatic nozzle to be extrapolated. The out come goal of this is to predict the travelling distance of the drop with time, allowing measurement position to be associated with a particular transient time and enable comparison

of the freezing time suggested by the PDA DSDs to those identical by the mathematical model. Hence, validating the PDA rate of sample measurement in freezing operations. The PDA velocity data used in this estimations were those measured at 60 mm or 38 mm for pneumatic and hydraulic nozzles respectively, see tables 5-18 and 5-19.

Table 5-18: Mean velocity data for a selected water drop sizes of a sprays produced by XA PR050 pneumatic nozzle at 3 bar gas + 2 bar liquid pressures, as measured at different height beneath the nozzle.

D(µm)	2			5	1	10	20		
Н	V	STDV	V	STDV	V	STDV	V	STDV	
60	76.27	16.13	73.87	16.59	78.88	15.36	106.55	19.07	
100	43.99	8.52	43.21	9.16	44.69	9.03	55.6	10.01	
160	26.94	5.65	25.36	6.53	25.04	6.24	26.24	5.83	
220	19.18	0	17.79	4.49	17.12	4.79	17.29	4.66	

D(µm)	2		5		10		20		
Н	V	STDV	V	STDV	V	STDV	V	STDV	
60	68.7	15.59	69.03	15.16	75.19	15.31	90.64	19.3	
100	36.54	9.56	36.22	9.1	37.65	8.91	42.66	9.03	
160	20.03	5.62	19.9	5.27	20.02	5.33	20.44	5.36	
220	13.53	3.89	12.88	3.89	13.17	3.55	13.21	3.64	

Table 5- 19: Mean velocity data for a selected water drop sizes of a sprays produced by WL0.25 hydraulic nozzle at 5 bar feed pressure, as measured at different height beneath the nozzle.

Water spray i	in ambient te	mperature T	=	20	°C				
D(µm)	20	)	50	)	10	0	150		
Н	V	STDV	V	STDV	V	STDV	V	STDV	
38	14.28	2.59	18.44	2.01	22.09	1.58	22.87	0.85	
68	11.79	2.46	14.48	3.13	19.95	1.25	22.4	1.05	
108	9.92	2.47	10.35	2.12	15.21	2.63	18.88	1.64	
168	9.33	2.37	9.27	2.22	13.84	1.38	17.85	1.92	

#### Water spray in sub-ambient temperature T =-45 °C

D(µm)	)	20	)	5	0	10	0	150		
Н		V	STDV	V	STDV	V	STDV	V	STDV	
	38	15.62	4.62	20.03	2.68	22.32	1.86	20.91	0	
	68	15.29	2.41	18.03	0.88	20.72	2.04	24.2	0	
	108	12.17	1.2	16.44	1.8	20.23	1.48	23.63	0	













**(B)** 






The time verses height relationships is derived as follows:

$$v = \frac{dh}{dt}$$
 Eq (5-23)

For time taken for a droplet to travel between two distances can thus be determined by:

$$t = \int_{h_0}^{h_i} \frac{1}{\nu} dh$$
 Eq (5-24)

The results of the of water spray drops mean velocity data measured by the PDA at different heights indicated in tables (5-18) and (5-19) were used to plot the inverse of drop mean velocity vs, distance, ambient temperature results, see figure (5-63). The best fits for the plots are a polynomial equation (intercept equal to zero) for the pneumatic sprays, and a power law equations for the hydraulic nozzle sprays. The time relation is then determined by integrating of equations (5-25) and (5-27) for the pneumatic and hydraulic nozzles respectively.

$$t = \left[\frac{ah^3}{3} + \frac{bh^2}{2}\right]_{h_0}^{h_i}$$
 Eq (5-26)

For the pneumatic nozzle spray

$$t = \left[\frac{ah^{(b+1)}}{(b+1)}\right]_{h_0}^{h_i}$$
 Eq (5-28)

Where the subscription  $(h_0)$  and  $(h_i)$  are the initial height and height at (i) time interval respectively, (a and b) are equation constants for the extrapolated equations listed in the table below fore each height

Height (mm)	Constants for of of spray proceeding of spray proceeding of the spray proceeding of the spray of	Constants for equations of spray produced by oneumatic nozzle		Constants for of spray pro hydraulic noz	r equations oduced by zle
	а	b		a	b
60	0.0931	0.2167	38	0.1713	0.268
100	0.1875	0.2147	68	0.1874	0.2966
160	0.3308	0.1936	108	0.2665	0.4878
220	0.6358	0.126	168	0.1328	0.3374



(A)



(B)

Figure 5- 64: Extrapolated time vs. height profile of selected drop sizes of water spray in ambient air produced by (A) XA Pr 050 pneumatic nozzle at 3 bar gas 2 bar liquid feed, and (B) WL 0.25 hydraulic nozzle at 5 bar liquid feed pressure.

From the obtained time equations (5-29) and (5-31) the drops travelling time along the chamber height was estimated for sprays of the pneumatic and hydraulic nozzle respectively, see figure (5-64). The results of the drops in a pneumatic nozzle sprays the travelling time reading from graph (5-64 A) indicates that droplets travelled more than 100 mm in a approximate time of 0.025 second, which is correspond to the maximum predicted freezing

time of a large drop at the lowest freezing gas temperature shown in figure (5-57). This explains the increase in the rate of attempted sample rejection by the PDA measurement of the spray as droplet where possibly frozen before reaching the measurement point.

## 5.7 Conclusion

The aim of this experimental chapter was the measure the spray size distribution and velocity using PDA spray measurements, as new approach in spray freezing process optimisation to producing a good size distributed, narrow, particulate as a precursor for freeze-drying process. The PDA data then used to model the spray freezing operation.

The spray characterisation was carried out in a specially constructed cylindrical chamber with vertical (removable) windows to permit PDA measurements to be made. The sprayed solution was pure water which was atomised using either a pneumatic or a hydraulic nozzle. A number of chamber temperatures were used (20, -20, -40 and  $-60^{\circ}$ C), which were stabilised by supplying a set ratio of liquid nitrogen and cylinder gas in each case. The measurement volume was located on the centreline of the spray at various distances vertically below the nozzle orifice (60, 100, 160 and 220 mm for pneumatic nozzle, and 38, 68, 108 and 168 mm for the hydraulic nozzle). Droplet size distributions were normalised with respect to the total number of droplets/particles detected by the PDA equipment. The characterisation of spray in sub-ambient temperatures was an innovative attempt to investigate the possibility of applying phase doppler anemometry characterisation to the spray freezing operations. The results obtained had a promising outcome in term of possibility of particle sizing. It was generally the case that a proportion of these droplets were rejected by the PDA software for the characterisation of size and velocity. Our hypothesis was that in some cases this could be due to the onset of drop freezing: the presence of a solid component within the droplet could interfere with the refractive scatter. If the nucleation/recalescence model for drop freezing is correct then the appearance of a significant quantity of solid would happen very quickly after nucleation.

The results of the study show that at a fixed chamber temperature the rejection rate increased significantly with increasing distance from the nozzle. Similarly it was found that dropping the chamber temperature also increased the rejection rate. An analysis of the normalised drop size distributions showed that in the case of the hydraulic nozzle the rejected drops (those *An Investigation of Spray-Freezing & Spray Freeze-Drying* 263

which disappear compared to the distribution at ambient conditions) were almost exclusively at the smaller end of the distribution, whereas for the pneumatic nozzle the "loss" of droplets was more uniform. A difference in behaviour between the two systems might be expected as the pneumatic nozzle injects a significant quantity of atomisation gas at ambient temperature into the spray which is able to shield the spray droplets from the low temperature of the chamber gas. Drop freezing may thus be more chaotic and depend on random contact with small pockets of low temperature chamber gas. Conversely, with the hydraulic nozzle the gas temperature can be assumed to be much closer to the chamber temperature. The results also shown a possible case of drop disintegration under sub-ambient temperatures. Drop agglomeration concept is rejected for the spray at ambient temperatures, but, it is still a concern in the spray freezing, as there is two possibilities of particles losing sphericity due to agglomeration or small drops acting as nucleators for larger drops.

A simple model of the freezing process was used to gain an order of magnitude estimate for the freezing time and distance travelled for droplets using diameter and vertical velocity data derived from the PDA experiments. The model confirmed that the distances and temperatures involved with drop freezing taking place were consistent with those observed.

This work therefore strongly suggests that the PDA technique can be used as a non-invasive probe of drop freezing in spray freezing systems, in addition to highly valuable correlated data for drop size and velocity.

# Chapter 6

Spray drying experiments

# 6.1 Introduction

The main objective of this chapter is an experimental comparison of three different drying processes, spray drying, cryo-spray-freeze-drying "Cryo-SFD" and spray freeze-drying "SFD". The aim is to assess effect of the operational conditions and method of processing on the end product characteristics from three different distinguished liquid concentrates (i.e. sucrose, coffee and whey protein).

The main advantages of the spray drying processes is the acceleration of heat and mass transfer by increasing the transfer area to volume ratio while keeping the product temperature in a controlled temperature (predetermined), well below 100 °C for food applications this range between 50 to 80°C. This makes this process an attractive method for drying materials that are sensitive to temperature, as well as enhancing the retention of the original properties to a maximum level possible. Heat damage to products is generally only slight, because of an evaporative cooling effect during the critical drying period and because the subsequent time of exposure to high temperatures of the dry material may be very short. In the spray freeze-drying the risk of thermal damage is almost non existing, but the complication of the process leis in the risk of sample collapse due to melting hence quality loss of the dried product. The processing time in the freeze-drying operations far longer than that of spray drying.

The mechanisms of moisture removal in spray drying and freeze-drying are described in the chapter 2, and here the comparative study of the results and process performance shall be evidenced. The spray drying feed materials are usually concentrated liquids as it is economically and qualitatively beneficial for the process and products simultaneously. Where as in freeze-drying the mass transfer is dependent on optimal formulation of the processed material to reduce the vapour diffusion. The increase in the solute content plays a role in increasing the particle sizing and density that can improve the powder collection and separation, finally improving dispersibility of product.

The aims are sub divided into two integrated parts:

Comparison of products dried using 3 different processing methods. Performing tests described in chapter 4.

Testing of spray freeze-drying rig that has been constructed. Emphasis that this is still in development stages. Lessons learned on operation for future modification.

The testing methods proposed for performing this assessing this experiments are illustrated for all materials in the flow diagram in figure 6-1.



Figure 6-1: The Experimental testing methods of the spray dried powders.

## 6.2 Spray drying experiments

## 6.2.1 Material and analysis methods

The concentrated solutions were prepared as reported in Chapter 4, section 4.2. The methods of sample analysis are also described in the same chapter, section 4.3.

## 6.2.2 Processing apparatus and operation conditions

## 6.2.2.1 Spray drying process

The concentrate was then spray dried using a computer controlled tall-form spray drier (Spray Processes, Bedford UK), fitted with a twin fluid atomiser. The outlet temperature control was regulated by variation of the liquid feed flow rate to suit the gas inlet temperature and flow rate. The product collection equipment is a cyclone with collection bucket. The set up for the spray operation of sucrose and whey protein drying are summarised in table (6-1). The drier is 12ft high, 4ft wide and 6ft long it has the following operational features

<ul> <li>Gas heating method</li> </ul>	Natural Gas
--	-------------

- Typical air flow-rate 600kg/hr (509.7 m<sup>3</sup>/hr)
- Flow configuration Co-current
- Atomiser air pressure 4-6 bar compressed
- Atomised liquid feed pressure Variable
- Pump type
   Peristaltic Watson-Marlow 510U
- Pump speed up to 60 %

Table 6-1: Summary table of the spray drier operation conditions for different concentrates.

	Sucrose concentrate	Coffee concentrate	Coffee concentrate + 0.33% acetone	Whey protein concentrate
Inlet temperature (°C)	$160 \pm 5$	$200 \pm 5$	$200 \pm 5$	$180 \pm 5$
Outlet temperature (°C)	75 ± 5	$95 \pm 5$	95 ± 5	$80 \pm 5$
Gas valve setting (%)	20	65	70	37
Pump speed (%)	30	30	30	30

The coffee concentrate spray freezing and or spray freeze-drying testing were to be analysed particle morphology SEM twice, one for the material inoculated with a volatile content and other for a none inoculated soluble coffee concentrate samples, due to the change in the processed liquid surface tension and viscosity upon the addition of the volatile component (acetone).

# 6.2.2.2 Cryo-Spray-freeze-drying process (Cryo-SFD)

The cryogenic spray freezing operation setup and the freeze-drier used process are described in chapter 3 section 3.4. The liquid concentrate were atomised using the XA Pr050 pneumatic nozzle at 3 bar gas 2 bar liquid atomisation pressure from  $(80 \pm 20 \text{ mm})$  height above the liquid nitrogen surface. The variation in height is due to uncertainty in the position of liquid nitrogen surface as liquids boils off. Samples were loaded into a BOC Modulo freeze-dryer connected to a 5 m<sup>3</sup>/hr vacuum pump from BOC Edward, supported with a 100 m<sup>3</sup>/hr vacuum pump from Werie Rietschle. The operation temperature of the condenser was -45 °C and system pressure 9-8 mbar.

Additional samples were also taken (whilst still in a liquid nitrogen slurry) to the Food Science Department at the University of Nottingham (Sutton Bonnington Campus) where they were loaded onto shelf based Modulo-dryer.

## 6.2.2.3 Spray-freeze-drying process (SFD)

This rig design and operation was described in chapter 3 section 3.3. However, the fluidisation operation was not preformed in current research operation. The spray nozzle used was XA Pr050 at 3 bar gas 2 bar liquid feeds pressure. The sample spray frozen in flowing sub-ambient gas (<1 m/s and temperature  $-45 \pm 5$  °C). The freeze-drying conditions were recorded every second and logged for process assessment.

# 6.3 Results

# 6.3.1 Results of the spray drying experiments

The spray drying of whey protein and coffee concentrates were successful operations, however the spray drying of sucrose concentrate failed. This was due to product sticking to the walls of the chamber. There was evidence that the atomisation of the spray was successful as sticky syrup was also found on the walls of the cyclone and the collection bucket, which indicates the spray was able to travel through the spraying chamber and cyclone.

The methods of spray dried powder analysis and calculations were described in details in chapter 4, section 4.4 and the summary of the results were presented in tables 6-2 and 6-3.

Dried Material	Sucrose concentrate	Whey protein	Soluble coffee	Soluble coffee inoculated
Measured Property				with acetone
Moisture content (%)	ng. Tier	6.99	8.06	5.72
Absolute Density (g/cm <sup>3</sup> )	dryi	1.25	1.03	1.136
Bulk Density (g/cm <sup>3</sup> )	the the	0.308	0.199	0.166
Pore Size Distribution (µm)	spra c to	None	None	None detected
	truch	detected	detected	
Particle Properties	d s			
Mean diameter ( $\mu$ m)	ltec ha ls.	27.74	28.56	30.38
Median diameter ( $\mu$ m)	resu trial wal	22.94	23.48	23.24
Std Div. $(\mu m)$	nate ne	19.36	23.01	24.61
Min. diameter size $(\mu m)^*$	odu e n /clo	3.48	1.279	2.42
Max. diameter size $(\mu m)^*$	o pr d cy	53.50	77.01	77.01
Distribution range ( $\mu$ m)	an Nc	50.02	75.73	74.59
Protein denaturation (%)**	*****	2.45	******	******
Volatile retention level (%)	*****	*****	******	12.63

Table 6-2: Summary of the spray dried particulate results.

The minimum and maximum particle sizes within 95% confidence line, described in section 4.4.7.1.2

\*\* Denaturation level estimated from the solubility fractionation as described in 4.2.7.2.1.

 Table 6- 3: Organic nitrogen content of the whey protein in the spray dried powder after dissolving and centrifugation by Kjeldahl nitrogen determination.

Tested Sample	Protein Content %
Non-separated 30% conc. Pre spray drying	84.3
Separated soluble whey 30% conc.	82.0
Spray dried whey Concentrate powder (WPC)	82.7
Soluble WPC separated from dissolving a 30% powder	69.2
Insoluble WPC separated	27.3



Figure 6-2: Cumulative moisture content loss of spray dried whey protein powder.



Figure 6-3: Cumulative moisture content loss of spray dried coffee powder.











(B)

Figure 6- 6: Spray dried whey protein particle size characteristics. (A) Particle Size distribution, (B) Cumulative distribution.



Figure 6-7: SEM images of spray dried soluble coffee.



Figure 6-8: Spray dried soluble coffee particle size characteristics. A= Particle size distribution, B= Cumulative distribution.











# 6.3.1.1 Spray drying results discussion

The dried powder physical properties are controllable to a certain size distribution, moisture content, density and morphology which will depend on the atomisation conditions and the physical conditions under which the water is removed, particle structure will depend on how the droplet solidifies, whether by dehydration or initial freezing. The particle drying rate depends on the temperature and air humidity to which it is subjected. The severity and duration of any heat treatment in drying affects levels of quality loss such as loss of volatiles, protein denaturation and structural deformation.

The droplet when released from the atomiser undergo solidification companied by a frictional forces that dictates the drying performance of the drops, which must be over come to achieve successful drying. The drop first solidify on the surface and then heat conduction vaporises the water internally so the particle either expand or explode to release the trapped water vapour, the drying kinetics of spray drying is described in chapter 2. In the drying mechanism the droplets velocity limits their growth when it is in the liquid form, at least in the spraying area of the chamber. Further down stream the drop solidify then it is prevented from neither growing nor caking, hence it is stabilised in size and shape, this was evidenced in the SEM pictures. The quality of the dried powders is related to the retention of internal structure and porosity and minimising the collapse and shrinkage of the particles.

The assessment of the dried particulate shows whey protein powder is denser, bulkier and with narrow distribution in comparison the coffee powder. This characteristic was a result of the viscosity, whey protein concentrate has a higher viscosity than coffee and therefore it has a narrower particle size distribution. The absolute density had recorded low values for the coffee powder as the shell cases of the particles are thinner than that of the whey. The value of the particle density is dependent on the solid surface maintaining the entity of the particle, in comparison to the bulk density which is relay on the interstitial gaps between the particles. The results in table (6-2) shows that the whey powder bulkier than coffee powder, this is explained by the more spheroid entity of the whey powder and its wall thickness. The particles of the whey powder are more orbicular shaped and intact sphere particles due to its liquid physical properties in particular viscosity and composition.

In general the moisture content measured for the particulates was higher than the accepted level of the dried particles. The spray dried coffee powder is referenced to have a 3% moisture content, and spray dried whey powder moisture content is variable with the type of the drying processing (ordinary, pre-crystallised, and non-caking whey powders) ranging from 3-6 %. The current results considered within the acceptable dryness level, since we are able to have a significant handling opportunity without caking or sticking of the particles.

The analytical study of spray drying results for the four material formulations exhibited variation in particulate properties depending the properties of liquid material and the processing conditions, and therefore the obtained results considered separately except the evaluation of the dryness of the particles.

#### 6.3.1.1.1 Sucrose

The failure of sucrose spray drying experiment was partly to be anticipated result due to the difficulty of drying sugar rich concentrate. It is a well-documented industrial problem an results from the low Tg of the sugar containing solutions. The glass transition temperature of sucrose is  $(T_{gsuc.} = 62 \text{ °C})$ , which is lowered by added water  $(T_{gw} = -135 \text{ °C})$  content in the concentrate to a measured value of -35 °C (chapter 4). Drying processes are likely to produce stickiness unless the air temperature is in the vicinity of the  $T_g$  or below (Blanshard *et al.* 1993; Roos 1998; Roos 2000). The process of the spray drying has an inlet air temperature of  $(160 \pm 5 \text{ °C})$  all the particle temperatures will be much lower than this due to the wet bulb effect. Most cases of the spray drying of sugar rich solutions preformed by having additives with higher  $T_g$  such as maltodextrin to increase the  $T_g$  in the solution till achieving significant crystallised or amorphous structure drying while the drops travel in the chamber. Das et al 2002, had reported cooling the crystallised dried particulate produced by low temperature spray drying to prevent them from sticking due to cohesion (Mani *et al.* 2002; Adhikari *et al.* 2004). However this requires either a large chamber or very small particle size for the spray to dry before contacting with the spray drier chamber wall.

## 6.3.1.1.2 Whey protein

Whey protein powder had more spherical shape particulate, and the evaporation produced some cenosphere powders, this occurs stir forming formulations where the shell remains moist whilst water evaporates from the centre (Masters 1991; Walton *et al.* 1999b). The pressure build up inside the particle also causes "blowholes" where the vapour is vented, see SEM images in figure *An Investigation of Spray-Freezing & Spray-Freeze-Drying* 279

(6-5). These images also reported a range of particle size distribution generated by the pneumatic atomiser used, though it is relatively narrow in comparison to the spray dried coffee produced using same atomisation pressures, 50  $\mu$ m distribution range (table 6-2). The powder is a cohesive and hygroscopic in nature, typical of whey proteins (Johonson *et al.* 1974; Masters 1991). The whey protein powder produced in this spray drying operation has particle sizes in a range of 50  $\mu$ m or less relatively non–spherical nor smooth surface particles, and classify this product in the semi-free flowing cohesive powder. The powder flowability is influenced by the shape, particle distribution, and surface moisture content and hygroscopic nature of the powder (Walton *et al.* 1999b).

The measurement of the drying effect on protein stability was assigned to the functional property of whey solubility. Whey is group of proteins that's  $\beta$ -lactoglobulin a count for its major constituent. It is a globular protein soluble in water and upon denaturation it loses solubility due to structural unfolding.  $\beta$ -lactoglobulin denatures by heat-induced reaction at 94.3 °C at 6.6 PH (Johonson *et al.* 1974; Fox 1992). The porosity measurement had detected no significant values of pore sizes presents, this confirmed the SEM images of finding of hollow particles with hard shell casing. During the porosity measurements the sample had higher moisture content and this caused by the whey powders hygroscopic characteristics of the milk and milk products powders.

The result of the nitrogen protein content determination of the soluble and insoluble constituent in the sample based on the Kjeldahl method (table 6-2) shows an ambiguity in the level of protein present. The protein content in the whey protein isolate was 84% that is dissolved in water and produced a concentrate contains 82%. This was spray dried and produced powder containing 82% protein in both native and denatured form. Dissolving this powder in water produces soluble and insoluble constituents, and when analysed for protein content using Kjeldahl nitrogen determination the results indicate values of 69% and 27% of soluble and insoluble proteins respectively. Here an important question come to surface, what is the nature of the remaining 30% and 70% content in the soluble and insoluble constituent of the whey proteins.

Thence organic nitrogen determination as a measure of protein denaturation did not provide a satisfactory answer for protein quantification. Hills 1986 had reported that the nitrogen soluble index (NSI) measurement is prone to error in assessing the protein content due to difficulties maintaining a repeatable testing conditions, therefore this method of assessment would be used

mainly to indicate the protein present in the source of whey powder and that in the pre dried concentrate (Hall *et al.* 1997).

The insoluble fractionation determined from the dissolving the spray dried whey powder produces a 2.5% of the dissolved sample in the insoluble form (table 6-1). This is a residue fraction of denatured protein resulted from spray drying concentrate of soluble proteins. The drying operation condition was as in the recommended literature of whey protein and milk product drying. However this denaturation is may not be a solely caused by thermal damage, as protein may denature due to high pressure processing such as atomisation (Johonson *et al.* 1974; Hall *et al.* 1997).

The result of protein denaturation measure presented a new statement in this research clarifying the fact of "*soluble content fractionation is a mean of drying process severity indicator*". Therefore the analysis of the protein functional property of solubility will be conducted by first "Kjeldahl organic nitrogen" determination in pre drying samples. Secondly, evaluating the denaturation level induced by drying process from "the fractionation of the soluble/insoluble constituent of the powders", both methods are described in chapter 4 section 4.4.7.

In conclusion spray drying of whey protein concentrate had produced powder with a hollow cenospheric, cohesive particles, with a diminished porosity and thermal denaturation level of 2.5% of the initial content.

# 6.3.1.1.3 Coffee

Two samples of coffee where spray dried and their product characterised, the first is soluble coffee concentrate and the second is same sample inoculated with volatile marker, acetone. The reason of such experimentation explained by the influence of the marker on the liquid phase concentrate thence particle characteristics. The result of the particulate reflects the variation mainly on the morphology of the spray dried coffee powder. Coffee is recognised as a skin forming material, which is predominantly hollow and soft with slight resistance to deformation, exhibiting plastic behaviour during deformation. In term of friability classification, it falls in the second category (F2), where the shell is more likely to tearing with no fragmentation of the overall particle (Walton *et al.* 1999a).

Comparing the moisture content measurements between the two variation indicates a better drying performance of spray drying coffee-acetone concentrate. This variation may be caused the presence of acetone reducing the resistance of the vapour diffusion through the dried layer.

Both spray dried coffee samples had relatively same particle size distribution, with one exception of the acetone inoculated powder had population of the large size increased this due to reduction in particle fragmentations during drying. The SEM image comparison shows a characteristic morphological difference in particle and integrity of the spray dried liquid concentrates variance. The images of spray dried coffee powder seems to exhibits a number of morphological features of spray drying (figure 6-6) such as shrivelling, fragmentation, bubbling and cenospheric shaping of hollow powder. Where as the coffee-acetone powder has much less fragmentation and cenospheric shaping of the powder (figure 6-7). It is from these SEM images noticeable that small particles remained mostly spherical and intact, neither fragmented nor shrivelled. This suggests the efficiency of drying when having smaller particle sizing and narrow distribution performance from the atomiser will help maintaining the morphology and size of the products. However, size reduction may influence the some qualitative characteristics such as rehydration of the powder, but there are secondary operations may help over come the problem, such as agglomeration. No porosity values recorded of the sample analysed by nitrogen adsorption measurements, which was expected finding.

The case of volatile loss during spray drying was evaluated by the percentage of volatile (acetone retained) in the produced powder. The result shows 12.6% of the inoculated acetone in the sample spray dried coffee was retained. In coffee spray drying usually less than 10% of coffee original volatiles retained by the end of the process. Though in this case study the sample was inoculated with a mass equivalent to 0.33 % (w/w) of the original concentrate (3300 ppm) and what has been detected in the pre-dried concentrate was 1376 ppm. This may be due the interaction of the acetone with other compositions in the coffee concentrate and results in change in the concentration properties. There after the retained mass recorded in the produced powder may be a result of that interaction. Walton and Mumford (1999) had reported role of the concentration, particle morphology and drying temperature on the volatile retention. He also reported that the skin formation of the particulate during drying will help retain some of the volatile constituent, and the loss is through dried layer is far less than that of the liquid dropt therefore most of the loss happens in the initial stages of drying. In this evaluation the quantification of the drying effect on the volatile retention was of interest, and we witnessed a

reduction to an evaluated level of 12.6 % retention thence 87.4% of all acetone is lost due to atomisation and drop evaporation (Desrosier *et al.* 1979; King 1979; King; Walton *et al.* 1999b).

The conclusion of coffee spray drying study succeeded in evaluating the loss of volatile for a comparative study against other processes of drying. Also the influence of composition of concentrate is highlighted and its influence on the morphological structure of the powder.

# 6.3.2 Results of Cryo-spray-freeze-drying process

The spray freezing operation and product transfer into the freeze-driers were successful, but the drying operations was doubting and required some adjustment. The samples of the soluble coffee and sucrose concentrates both collapsed in BOC modulo freeze-drier, and they were also tested in the drier at Sutton Bonington Campus (Nottingham university) and the sample also collapsed, figures (6-11) to (6-13) shows a selection of these samples. Where as whey protein concentrate were successfully cryogenically spray frozen and dried in both driers, and the results summarised in table (6-3) and figure SEM images of the particulate are of the sample dried in Sutton Bonington campus freeze-drier.



(A)

(B)

(C)

Figure 6- 11: Collapsed freeze-dried materials, (A) cryo-SFD sucrose Module-freeze-drier; (B) Collapsed SFD whey powder Modulo-freeze-drier; (C) Collapsed cryo-SFD Sutton Bonington drier.



Figure 6-12: SEM images of collapsed Cryo-SFD coffee (Sutton Bonington drier).



Figure 6-13: SEM images Collapsed SFD whey (Modulu-freeze-drier).

 Table 6- 4: Summary of cryo-spray-freeze-dried whey powder.

Dried Material Measured Property	Whey protein	
Moisture content (%)	2.92	
Absolute Density (g/cm <sup>3</sup> )	0.43	
Bulk Density (g/cm <sup>3</sup> )	0.29	
Particle Properties		
Mean diameter (µm)	27.74	
Median diameter (µm)	22.94	
Std Div. (µm)	19.36	
Minimum diameter (µm)	3.48	
Maximum diameter (µm)	53.50	
Distribution range (µm)	50.02	
Powder solubility (%) (measure of protein denaturation)	Complete dissolution	



Figure 6- 14: Moisture content of Cryo-SFD whey protein.









Chapter 6



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Figure 6- 17: SEM images of Cryo-SFD whey powder produced in Sutton Bonington freezedrier.

## 6.3.2.1 Cryo-SFD results discussion

Coffee and sucrose particulate samples both collapsed in the BOC Modulo freeze-drier that was vacuumed by the duty of two vacuum pumps simultaneously (BOC Edward 5 m<sup>3</sup>/hr to 0.02 mbar and Rietschle 100 m<sup>3</sup>/hr), to help removing the large volume of liquid nitrogen. It was decided to try then freeze-drying in a different freeze-drier the Food Science Department at Nottingham University. The results was equally same in both driers.

The collapse of the spray frozen coffee and sucrose particulate was not totally un expected results as these materials have low  $T_g$  values, (coffee = -24.92 °C and sucrose = -33.68 °C), in comparison to the whey concentrate which has a high collapse temperature (closer to its melting point), see chapter 4 section 4.3.6. In addition to this the concentration of the solute in the freeze-dried material had a probable effect by resisting the vapour diffusion and lowering the rate of mass transfer. This is a well reported concern of the freeze-drying operation success is dependent on the dried material formulation (Goldblith *et al.*; Mellor 1978; Jennings 1999; Oetjen 1999). Also the rapid freezing had resulted in two structural resistance to the vapour diffusion, the first being the outer shell hardening leading to a less number of pores extending to the surface, and the second is the small ice crystal reducing the pore size with poor networking of the channels, see figure (6-17). In both cases the slowing of the rate of sublimative cooling of the particulate in the freeze-drier that resulted in the increasing the material temperature to its melting temperature and leading to the sample collapse.

The results of whey powder shown in table (6-4) indicated a sufficient level of sample dryness after a period more than 24 hrs, with a moisture content less than 3 %. The particle size distribution shown in figure (6-15) showed an increase in the mean drop size of the spray generated comparing to that of water, sucrose and coffee (measured by PDA-Chapter 5). There are two possible causes of this size increase, assuming no volume change occurs during sublimation or an particle damage in due course. The first is the physical properties of liquid whey concentrate (this was not tested by PDA), the effect of these properties can be confirmed when comparing this graph results with that of spraying in sub-ambient gas (next experiment). The second possible effect is the rapid cooling of the liquid nitrogen reducing the drop disintegration capacity, which is most influential in my opinion. The particle size distribution shown in figure (6-15) shows a limited degree of possible swelling due to diffusing of the

suspending liquid (iso-butyl alcohol) through the pores of the particles. The third sample run had an identical shift in towards the large size distribution.

The SEM particle morphology analysis of these cryo-SFD whey powders are shown in figure (6-16) and shows:

- hardened particle outer surface,
- · less surface porosity compared to next sample of SFD drying
- cracking and wizened surfaces
- · non-spherical and irregular shaping of the particles
- wide spread size distribution
- fine internal porous structure

These images brings the efficiency of cryogenic spray-freezing operation that is intended for freeze-drying operations to the spot light of being excessively harsh, and to a certain extent have a negative effect on the process performance and product quality. Most of spray freeze-drying operation research in pharmaceutical and ceramic industries were carried in this style of operation (McGrath *et al.* 1992; Sonner). The rapid rate of freezing of the liquid nitrogen had certainly in addition of affecting the particulate shape has produced very small ice crystal sizes and resulted in a finer pore size.

This fine porosity generally reported as structural matrix resisting the vapour diffusion during sublimation (Goldblith *et al.* 1975; Mellor 1978; Jennings; Oetjen 1999), but not mentioning the influence of the external surface porosity on the rate of sublimation and vapour diffusion.

The solubility test indicated all the powder was dissolved in water, with out rapid mixing, and the solution produced appeared identical to the soluble whey concentrate prior to processing. The results thus suggests that no denaturation resulted from this cryogenic process.

In conclusion the cryo-SFD process performed and produced only one type of powder suitable for process performance evaluation comparison.

# 6.3.3 Results of SFD process

# 6.3.3.1 Operation of the spray freeze-drying rig

During to operation of this spray freeze-drying rig there were some operational and process control difficulties were reported that required a significant period of commissioning. Due to the time limitation of this research and considering the difficulties of freeze-drying sucrose and coffee materials encountered in the previous section, only one sample of whey concentrate was spray freeze-dried under no gas flow condition. The operational problems were reported in chapter 3, section 3.3.5.4, here a brief description was listed

- Leak of outside air into the system. These were successfully plugged but did require removing the recirculation fan which was a large source of leaks.
- The failure of cyclone temperature control.
- Failure of particle separation by the cyclone, most particles were sucked out of the system into the extraction vent.
- Spring disc failure due to mechanical damage during operation caused by an excessive pressure drop.
- High pressure drop across the bed sintered mesh.
- Excessive heat.
- Lack of insulation of pipe work. This was deliberate as insulation would interfere with modifications to this rig makes modification difficult.

The solution of removing the fan, problem (i), required the dryer to be operated in alternative mode- namely by closing the butter fly valve between the  $N_2$  inlet and the vacuum valve and then using  $N_2$  gas from the dewer as the fluidisation gas. It was decided to operate the freezedryer ina pure vacuum mode. Problems (ii & iii) were eliminated by removing the cyclone unit and loading the particles into the freeze-drying vessel manually, after been collected in a pre cooled polystyrene box. The spring disc part was removed and the sintered mesh was replaced with more open type especially made for the task. The (v) problem overcome by adding cold nitrogen into the system to cool it down while purging the system from humid air entered during sample loading. The last problem was solved by cooling the vessel metal externally with liquid nitrogen for a duration of 30 min till the system established in and pressure to prevent collapsing the sample. The fan assembly was one of the complex parts of the rig assembly and needs to be remade, but the time required to do this was beyond the time frame of the project. The removal of the fan meant that the system could not be run in the intended mode, but it was instead run on once through mode using nitrogen from the inlet. However a problem emerged that stopping the liquid nitrogen flow for any period of time meant that heat leakage into the supply pipe caused the feed to rise to too high temperatures to be admitted to the freeze-drying vessel without causing collapse in the sample. This is a problem that needed to be addressed. It was observed, however, that a satisfactory bed temperature was maintained by simply running the rig under high vacuum as in conventional freeze-drying, see figure (6-22). This was enough to produce a very good quality product.

The system was operated for a duration of more than 69 hours to assure the dryness of the sample since the spring disc measurement was removed, however the operation parameter log shown in figure (6-23) indicates the dew point temperatures almost reached an equal temperatures after 40 hours of operation, significant drying (at least primary sublimation) was reached.

# 6.3.3.2 Spray freeze-dried whey products

The resulting powder was analysed as above and the result displayed in table (6-5) and figures (6-16) to (6-23).

Table 6- 5: Summary data of the SFD whey particles.

Dried Material	Whey protein		
Measured Property	triney protein		
Moisture content (%)	4.11		
Absolute Density (g/cm <sup>3</sup> )	0.41		
Bulk Density (g/cm <sup>3</sup> )	0.22		
Particle Properties			
Mean diameter ( $\mu$ m)	45.87		
Median diameter ( $\mu$ m)	49.41		
Std Div. (µm)	17.65		
Minimum diameter ( $\mu$ m)	6.59		
Maximum diameter ( $\mu$ m)	64.19		
Distribution range ( $\mu$ m)	57.60		
Powder solubility (%)	Complete dissolution		
(measure of protein denaturation)	Complete dissolution		















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Figure 6- 21: SEM images of SFD whey protein powder.



Figure 6- 22: Particle bed temperature log of the measured by type "T" thermocouple.



Figure 6- 23: Dew point temperature log of the SFD operation measured by capacitance humidity sensors (Ex. Michell instrument Ltd) at two locations before the dried particle bed (inlet dew point temperature) and near the evacuated gas outlet (outlet dew point temperature).



Figure 6- 24: Freeze-drying chamber operating pressure measured by gauge pressure transducer (Ex. Omega Instruments).

#### 6.3.3.3 Discussion of the SFD process results

## 6.3.3.3.1 Process performance

The overall evaluation of the newly developed rig of a novel spray freeze-drying concept had produced an encouraging results, being capable of successfully freeze-drying a material (Whey protein) with an excellent characteristic properties. Unfortunately it was not possible to test the acceleration of the freeze-drying by fluidisation freeze-drying, or to monitor sample mass with time. Therefore in this section a discussion of the problems and obtained finding were discussed.

• The primary aim the SFD process was to design an accelerated process capable of operating in shorter time than conventional freeze-drier. The results obtained shows a duration of drying was at least of a 40 hours, figures (6-22) and (6-23), but this was not carried in a non accelerated drying process. The freeze-drying gas flow intended in the fluidisation process a proven statement of acceleration in the freeze-drying process by many researches (Woodward 1963; Boeh-Ocansey 1983; 1988; Mumenthaler *et al.* 1991), also others whom included the low vacuum (Mellor 1978) and convection heat and mass transfer could accelerate the freeze-drying rate (King *et al.* 1968). Thence the statement of the SFD process being accelerate process is not rejected until it is proven experimentally other wise.
- The system operation was performed under high vacuum as seen in figure (6-23), for the purpose of achieving a successful drying operation of no collapse, and the results was rewarding. Though if there was an adequate temperature control of the system, induced by sufficient insulation and steady gas flow temperature regulation, it would be possible to operate at higher pressure and preventing the material collapse. The system internal absolute pressure had shown a record of a negative reading, not possible, this was due to the long time duration operation and the measurement was based of subtracting the atmospheric pressure from a gauge pressure reading. But the atmospheric pressure is changing with time, and this requires an mean of continuous log of the atmospheric pressure measurement to synchronise sufficient reading. The first part of the graph in figure (6-23) shows an increase in pressure to above atmospheric this was a case of post loading cooling and purging of the freeze-drying vessel. In overall evaluation of the vacuum unit operation was sufficient to maintain operational pressure.
- During freeze-drying the particle temperature had shown an increase that could have lead to
  melting and sample collapse raise, that required and external cooling to helps the temperature
  maintenance inside the system. Though after a period of 1-2 hours this temperature rise had a
  steady temperature level, indicating the point of sufficient sublimative cooling presence in
  the system.
- This temperature increase raise a question about the sublimative cooling power present inside this operation system. The answer lays in the proposed fluidisation freeze-drying gas flow, during fluidisation freeze-drying the gas feed would provide the lacked cooling power needed to maintain the sample solid state. Though one may argue that that during freeze-drying the continuous cooling may slow the secondary drying stage, the answer comes as the operation will predict the end of primary sublimation stage and then the gas flow temperature raised to a level maintaining the solid structure and in the same time aiding the dsorption mass transfer of the secondary drying phase. It is a similar concept of conventional freeze-drying, but the difference would be the convective heat and mass transfer, without the risk of melting caused by the sublimation latent heat supply from heating.
- The dew point temperature  $(T_{dp})$  log of the drying operation was approached equal reading after approximately 34 hours of drying time. This graph was an adequate to high light the end of the drying process in all but not pin-pointing the exact time in this experiment and it aggress with the reporting of the findings researchers in the field (Roy *et al.* 1989; Baradat *et al.* 1993; Genin *et al.* 1996). Thence presence of internal measure of the actual bed mass would have been a complementing tool for drying process end determination, pointing the

end of primary sublimation end point by both and the secondary sublimation by achieving the moisture content desired, Though, the spring disc device was terminated due to operational damage of caused by high vacuum extraction power. However, the concept is viable and can be re-introduced once the system design and operation is fine tuned.

#### 6.3.3.3.2 Product quality evaluation

The produced whey powder had was reasonably dry and had close absolute and bulk density to that of produced by cryo-SFD process, indicating almost matching drying and performance. The comparison of the physical property data for the SFP and the spray dried whey powders show differences in both absolute and bulk density. The bulk density values of spray-freeze-dried particles are approximately 25% less than that of spray dried particles. This may be due to the lack of sphericity of the spray-dried particles and the likelihood of some shrinkage of the outer shell during drying. Spray-freeze-dried particles are much more likely to keep the original dimensions of the droplet/particle immediately after atomization.

The absolute density values show a large (factor of 3) difference between spray-freeze-dried and spray dried particles. These values require a degree of caution in their interpretation as the inclusion of sealed, but partially hollow particles will lead to an effective increase in measured sample volume and thus a lowering of the measured absolute density. However, just one single hole is all that is required to allow the penetrating gas access to a cavity. It may be that the hollow shell morphology of the spray dried particles makes it vulnerable to a single hole being all that is required to fill the whole internal void space with gas. The more sponge like microstructure of spray-freeze-dried particles may not have a perfect interconnectivity of pores and so a single surface hole may then not lead to complete filling of the internal voids of the particle.

The particles produced by SFD seems to have large mean diameter, and small particle distribution size in comparison to that of the cryo-SFD process, table (6-5). This may sound contradictive, but it can be explained from the shape of the particle size distribution curve, which shows a sharp peak for particles between 50 to 80  $\mu$ m. The images shows some "built in" agglomeration that reduced the number of the small particles and increase the size of large ones. In comparison to spray drying powders they were produced by different nozzle and their drying process endured size changes, therefore it was not logic to compare the particle size distribution.

rough, porous topography. The spray-freeze-dried particles showed no evidence of protein denaturation (from solubility measurements), whereas a small fraction (2.5%) of spray dried powder was insoluble. However the rig requires further operational testing and for quantitative measure of performance and process control, followed by experiments of producing different materials and of sugar rich and aromatic, or ceramic concentrates, finding the optimum drying formulation and conditions.

## Chapter 7

## Conclusion and recommendations for future work

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#### 7.1 Summary and conclusion

Drying is an important process for a variety of industries such as pharmaceuticals, food, and chemicals. Drying results in products with low bulk density, good shelf stability, economical, and in some cases unique structural qualities. Of various drying methods available, freezedrying is the most suitable for heat sensitive products that are susceptible to thermal degradation and confers a porous structure on the material resulting from the voids left after sublimation of the ice crystals. Freeze-drying is currently used mainly for high value products due to the high manufacturing cost implicated by the high capital and operational cost. The operation time of such drier may take several hours.

This thesis has examined the spray freeze-drying process by designing and constructing experimental rig composed of co-current spray freezing chamber connected to a freeze-drying vessel, operate-able under atmospheric, vacuum, and intermediate pressures. The rig was operated to produce whey protein powder and examine the physical, functional, and morphological properties of particulate materials and compare to those obtained from spray drying, and cryo-spray freeze-drying. Significant differences in morphology were observed between spray dried and spray freeze-dried particles.

The spray-freeze-dried whey show a different porous microstructure, with enhanced pore sizes in comparison to cryo-spray freeze-dried powders due to lower rate of freezing. The powder bulk density were approximately 25% less than that of spray dried particles, due to sphericity of the particles and surface smoothness. The absolute density values appears noticeably smaller from that of the spray dried powder. The powder had a good solubility comparing to the spray dried samples were a slight increase in insoluble matter of the powder, likely to be caused by thermally induced denaturation of the whey proteins. No insoluble matter could be detected in the spray-freeze-dried powder.

Spray freezing is a critical to the structure of the resulting particles as the distribution of the ice crystals directly corresponds to porous region in the dried product. The connectivity of the ice crystal pores also important to the kinetics of the sublimation process. Spray freezing has therefore been studied in some depth using Phase Doppler Anemometry (PDA) to characterise the spray, by obtaining insitu drop sizes and velocities of the spray bulk. This is used to provide data for a simple model of spray freezing.

PDA experiments were carried out in an attempt to produce select the most uniform size distribution spray from the spray operations and conditions available. The technique had successfully measured the particle size distributions and velocities gaining the advantage of comparing the size distribution of sprays at ambient temperature with those of sub-ambient conditions, and indicating the occurrence of freezing existence prior to the measuring point. A spray-freezing model was developed from modifying the Pham (1984) freezing model incorporating the recalescence step from Hindmarsh (2003) model for single drop freezing. The current model shows an agreement of freezing time prediction with the results of sub-ambient spray freezing characterisation, the predicted time matches the rate of increasing the sample rejection rate of the PDA measurements, which are suggestive of particle solidification. Also the model shows that droplet freezing is influenced by the droplet diameter, velocity and freezing gas flow rate.

The PDA analysis of the spray had produced a tremendously valuable findings to spray freezing characterisation and is a pioneering step in spray freezing measurement. The main findings can be described individually as follow:

- Drop size distributions produced for sucrose and coffee solutions were similar to that
  of water with only a mild increase of 1 % to 3 % in the mean size.
- The PDA velocity data of the sprays shows that the particles passing a point appears to be travelling at similar velocities irrespective of the particle size. The velocity profiles estimated were characteristic to the type of spray, typically "S" curve for the pneumatic spray, and "tick mark" like profile for the hydraulic sprays. The Standard deviation of these velocities for a drops from a same size class, width of 1 µm, were typically 20 to 40% of the absolute velocity.
- The data also show an apparent increase in the rejection rate for the sub-ambient measurements, particularly at lower drop sizes. This is due to possible drop freezing producing predominantly reflective burst signals, or, due to the drops agglomerations or both cases. The SEM images obtained for a spray freeze-dried whey powder reported the possibility of agglomeration during the whole spray freeze-drying process. Though, this does not rule out the first possibility.
- The freezing models were applied to estimate the freezing times, assuming the gas
  phase temperature surrounding the drop was the same as the chamber temperature.
  The model was applied using three different methods of slip velocity estimations

- A constant slip velocity of 10 m/s, of the same order of magnitude as the standard deviations of the PDA measurements. The results were an optimistic prediction of the droplet freezing time.
- At constant terminal velocity, the results were a pessimistic prediction of the freezing time.
- Using the droplet deceleration model, although, this model has been shown to be inaccurate for droplet absolute velocity, it could serve well as a realistic model for droplet terminal velocity.
- Despite the wide range of velocity estimates, the heat transfer coefficient is only a weak function of the slip velocity and hence the freezing times were comparable, within a factor of 2, was an intermediate between the other two methods.
- Experimental freezing time were estimated from the PDA velocity data to calculate the average time for the droplets to reach the distances, from the nozzle, used as a measurement locations in the PDA experiments. The results predicted that the smaller drops would be frozen before these locations were reached.
- The comparison of the PDA data to the model of the particle motion and drop freezing. The results hints that the single drop model was a poor predictor of the droplet absolute velocity. The assumption of gas velocity is zero in this model is an under estimate, particularly since the fines in the spray are shown by the PDA measurements to be moving at a significant speeds in the chamber. This gas velocity is caused by the atomisation gas jetting in the chamber for the sprays produced by the pneumatic nozzle. Whereas for the sprays of the hydraulic nozzle, it appears that the gas is predominantly accelerated by the drag force of the decelerating droplets according to Newton's 3<sup>rd</sup> law.

#### 7.2 Future work and research

This thesis reported a number of operational problems of the spray freezing and freeze-drying chambers that require further development.

#### 7.2.1 Spray freezing

In this research spray freezing appear to have been detected by the analysis of the data obtained from refractive light beam scatter. A more comprehensive measure would be to simultaneously measure both refractive and reflective light scattering. In theory this would monitor the disappearance of the "refracted scatter" of the droplet burst and appearance of the

"reflected scatter" simultaneously. This would require a second PDA receiver unit. This would make it possible to distinguish between the droplet freezing and particle agglomeration, which is cannot be differentiated using the current set up of refractive scatter only.

There is some doubt over the validity of assuming a constant gas chamber temperature due to the warming effect of the droplet on the gas, and in the case of a pneumatic nozzles, of the introduction of ambient temperature gas through the atomiser. A recommendation for future work is to measure the temperature profile of the spray gas in the centre of the spray in multiple points such as by using a "temperature probe tree". This is composed number of thermocouple junctions positioned at an accurate distances in vertical positions at the best centre of the cone, starting from the disintegration point. Performing such measurement under nominally identical conditions of the spray freezing will help profiling the temperature change and allow more accurate modelling of the freezing time estimation.

The nucleation temperature prediction is dependent on the kinetics of the nucleation in the drops. Therefore it would highly recommended to establish a kinetic/statistical model of nucleation linking it to the freezing point depression caused by the solutes for freezing of aqueous solutions. Nucleation temperatures where an unknown input parameter to the freezing models and some independent measurements would be valuable.

#### 7.2.2 Freeze-drying

The design of the current freeze-drying vessel was adequately successful in operating the freeze-drying under vacuum. However, problems were reported in the operation of some parts such as the spring disc, the circulating fan, and nitrogen gas feed, which require rectifying before the rig can be used to its full potential.

The use of the spring disc is a novel mean of online measurement of the rate of heat and mass transfer in the freeze-drying operations. Previously Roth et al. (2001) had used a microbalance to measure the drying rate of samples in a vial inside a freeze-drier. The proposal of this research was to determine the mass transfer rate of an entire freeze-dried bulk in continuous measurement. The spring disc was chosen to maximise resolution at the limit of the mechanical integrity. Although the principle of the disc did work, it was not strong enough to survive the operation. A stronger spring disc with lower resolution is needed for future work. The recommendation for this proposal is to test the principle on an atmospheric fluidisation

drying rate measurement, and then repeat the test at low-pressure fluidisation and ambient temperature conditions, to determine the ideal fluidisation conditions under low pressures. Finally perform the test under the freeze-drying condition of interest.

For future operation of the freeze-drying vessel the investigation of low pressure fluidisation freeze-drying is an optimum goal to accelerate the freeze-drying process. The outcome of the current research had laid the fundamentals for its future operation.

A number of areas of study can be further investigated

- The effect of freezing temperature on the droplet structure and shape as found in the freeze-dried samples of the cryo-spray freeze-dried and spray freeze-dried samples.
- The effect of freezing rate on the rate of sublimation for cryo-spray-freeze-drying and spray freeze-drying processes.
- Establishing operating conditions to enable freeze-drying of materials with low collapse temperature, such as sucrose and coffee solutions. Investigating the effect of variables other than temperature on the collapse phenomena.
- Looking at the effect of the processing method on the product quality. For example with volatile retention the following aspects can be considered:
  - Volatile loss in the gaseous spray freezing zone, by sampling both the gas and the spray, to determine the volatiles content and comparing that to the spray drying operations,
  - o Volatile loss in vacuum spray freeze-drying, and
  - o Volatile loss during fluidisation freeze-drying.
- Investigating the biological material stability in spray freeze-drying comparing to cryo-spray freeze-drying, examining the rate of freezing effect on the biological material molecular structure.

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## Appendix

## Spring disc and bending strain calculations

#### The design of the fluidised bed spring disc

The load of the fluidised bed vessel and added mass of the frozen particles creates stress on the supporting spring disc shelf that would lead to bending. This stress would change with the mass change of the added particles during drying by sublimation. It is possible determine this stress from forces caused by the load, which would be monitored in term of tensile or compression stresses on the spring disc.



The cyclone separator separates the fluidised bed vessel from the spray-freezing chamber; they are connected via a vacuum-sealed butter fly valve. The vacuum operation kept inside the fluidisation vessel only. The dimension of this cyclone were

$D_{cy}$	= 300 mm
H <sub>cy</sub>	= 300  mm
H <sub>cone</sub>	= 420 mm
$\mathbf{D}_{\text{outlet}}$	= 136 mm
$\mathbf{D}_{inlet}$	= 80 mm
	D <sub>cy</sub> H <sub>cy</sub> H <sub>cone</sub> D <sub>outlet</sub> D <sub>inlet</sub>

The fluidisation vessel

Height	H <sub>p. vessel</sub>	= 270	mm
Inner diameter	$\dot{\mathbf{D}_{in}}$	= 164	mm
Wall thickness	t p. wall	= 3	mm
Polycarbonate material density	polycarbonate	= 1.2	g/cm <sup>3</sup>

It is a clear polycarbonate tube acting as the fluidisation compartment inside a vacuum vessel. The walls of this vessel was drilled with a series of 5 mm ID holes (1 cm) apart a long lines of 150 mm from the top edge and all around the circumference. These holes are the fluidisation gas outlets; a fine cloth loosely attached from the top until a height just above the bed will filter the gas. A stainless steel sintered mesh was attached to this polycarbonate tube with; it has the following dimensions listed below. Not all the sintered plate was used; the dimensions were cut to fit the polycarbonate tube.

Thickness	t <sub>sinter</sub>	=1.5	mm
Diameter	$\mathbf{D}_{sinter}$	=179.5	mm
Stainless steel density	$ ho_{sinter}$	=4610.3	kg/m³
Weight	Wsinter	=0.175	kg

The vacuum vessel design shows the mounting of the fluidisation compartment centrally on the spring disc.



#### The Spring Disc

The spring disc is an annular metal plate made of 316 stainless steel supported at the outer periphery on to a 10x10 mm circular fixed shelf. The spring disc secured in position, 2 mm away from the vessel wall, by circular disc 10x5 mm bolted to the lower shelf. The strain measurement circumference on the spring disc chosen 2-3 mm away from the outer porphyry. The dimensions of the spring disc are

Spring disc outer diameter	D <sub>s.outer</sub>	= 300	mm
Spring disc inner diameter	D <sub>s.inner</sub>	= 164	mm
Spring disc material thickness	X s.	= 0.1	mm

The specified dimensions of the strain measuring circumference, gauge positioning circumference and the loading area (displayed on the second diagram) were as follow

The strain measuring radius is	$\mathbf{r}_{strain}$	· = 136	mm
,	a	= 140	mm
	b	= 82	mm
	с	= 10	mm
	d	= 5	mm
	e	= 10	mm
	f	= 20	mm

#### **Considered** assumptions

- 1- The plate is flat, horizontal and uniform thickness with a homogeneous isotropic material.
- 2- The thickness is NOT more than (1/4) have the least transverse dimension.
- 3- The maximum deflection is NOT more than (1/2) have the thickness of the plate.
- 4- All forces loads and reactions are normal to the plane of the plate.
- 5- The plate is NOT stressed beyond the elastic limit.
- 6- The fixture of the spring disc is that stated in case 1e (Roark's Formula book, pages 398-402) (Young 1989)

#### Calculations of the Fluidised bed Load

The total load placed on the spring disc is that of the polycarbonate fluidisation tube with the attached sintered mesh. Adding to that the total mass of the sample dried and extra 10% mass for safe guard operations. These masses are

#### The polycarbonate cylinder

 $\begin{array}{ll} V_{p, \mbox{ fluidisation}} &= 4.25 E{-}04 \ m^3 \\ \rho_{polycarbonate} &= 1200 \ kg/m^3 \\ M_{p, \mbox{ fluidisation}} &= \rho V &= 5.10 E{-}01 \ kg \end{array}$ 

#### The Sintered metal

 $M_{sinter} = 1.57E-01$  kg

#### Mass of the processed sample

The processed sample when added to the vessel is 250 gram, on a wet bases as frozen particles.

 $M_{ice} = 0.25$  kg

#### Total mass of the fluidisation compartment

The mass of the fluidisation compartment is the sum of the above three masses, and 10% mass added to was added as for assurance of the disc tolerance of the load

 $M_f = 1.01$  kg

#### Initial bending load or force

The bending force intended for measurement are the result of the gravitational force caused by the fluidised bed mass. The variation of the moisture loss with time during drying, can detected as a for in the bending force variation. Thence calculating this force at three anticipated mass values of the fluidised bed when first empty, then filled with wet frozen particle bulk, and finally filled with dry particulate bulk can provide the initial specification of the strain gage size and positioning on the spring disc. The bending forces are calculated as follow

 $\begin{array}{ll} F_{\text{initial load}} & = M_{\text{f}} * g \\ F_{\text{initial load}} & = 7.85 \text{ N} \end{array}$ 

The maximum force applied during freeze-drying is when the bed is filed with 250 g ice particles. Thence this force is equal to

 $F_{drying max} = 9.89 N$ 

The ice powder contained 50% water content reduced by 99% less moisture the powder mass is reduced to 0.12625 kg. Then, the minimum load force applied when 99% of ice is sublimed

 $F_{dryingmin} = 8.68 N$ 

#### Bending stress and deflection calculations

The fluidised bed load was position centrally on an annulus area of the spring disc (g) 5 mm wide. This loading area was thence deducted from the dimensions of the spring disc. The material of disc is 316 stainless steel.

Sstainless steel	= 8000	kg/m³
E <sub>Stainless steel</sub>	= 1.96E+11	N/m <sup>2</sup> Young's modulus
Gstainless steel	= 8.70E + 10	N/m <sup>2</sup> Shear modulus
Ystainless steel	= 0.000012	°C <sup>-1</sup> Thermal expansion coefficient
$\Phi_{ ext{stainless steel}}$	= 1.12E+09	N/m <sup>2</sup> The yield or 0.1% proof stress

The value of the stress should not exceed the value of the yield stress.

$$y = y_b + \theta_b r F_1 + M_{rb} \frac{r^2}{D} F_2 + Q_b \frac{r^3}{D} F_3 - w \frac{r^3}{D} G_3$$
 Eq (B-i)

$$M_{t} = \frac{\theta D(1 - v^{2})}{r} + vM_{r}$$
 Eq (B- ii)

$$\theta = \theta_b r F_4 + M_{rb} \frac{r}{D} F_5 + Q_b \frac{r^2}{D} F_6 - w \frac{r^2}{D} G_6$$
 Eq (B- iii)

$$Q = Q_b \frac{b}{r} - w \frac{r_o}{r} \langle r - r_o \rangle^0$$
 Eq (B- iv)

$$M_{r} = \theta_{b} \frac{D}{r} F_{7} + M_{rb} F_{8} + Q_{b} r F_{9} - w G_{9}$$
 Eq (B- v)

$$v = \frac{E}{2G} - 1$$
 Eq (B- vi)

$$D = \frac{Eh^3}{12(1-v^2)}$$
 Eq (B- vii)

The deflection (-ve) in the down ward direction, its unit is (m)

w = the circumference of the loading area

#### Strain at initial loading calculation (empty)

Finitial load	= 7.85	Ν	
Adisc	= 4.05 E - 02	m²	
Ι	= 2.66E-04	$m^4$	
W	= 14.70	N/m	
ν	= 0.13		
D	= 0.02		
$M_{rb}$	= 0		
$Q_b$	= 0		
Уа	= 0		
$q_a$	= 0		
Уь	= -3.84E-02		
$q_b$	= 8.98E-01		
$M_{ra}$	= -4.65E-01		
Qa	= -8.93E + 00		
Ymin	= -4.68E-03	m	Displacement distance

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θ	= 1.09E-01	rad.	Displacement angle
$M_r$	= -4.40E-01	Nm/m	Radial moment
$M_t$	= -4.25E-02	Nm/m	Tangential moment
Μ	= 4.42E-01	Nm/m	Total moment
Q	= -9.19E+00	N/m	
O <sub>min</sub>	= 2.65E + 08	N/m²	Minimum bending stress of the fluidisation load
Emin	= 1.35E-03	strain	Minimum strain caused by the fluidisation load

#### Strain at maximum loading (full ice particles)

<b>F</b> dryingmax	= 9.89	Ν	
$A_{disc}$	$= 4.05 \text{E} \cdot 02$	m²	
I	= 2.66E-04	$m^4$	
w	= 18.53	N/m	
ν	= 0.13		
$m{D}$ . The second s	= 0.02	:	
$y_b$	= -4.84E-02		
$q_b$	= 1.13E+00		
$M_{ra}$	= -5.86E-01		
$Q_a$	= -1.12E+01		
Ydrying max	= -5.90E-03	m	
$\theta$	= 1.38E-01	rad.	
$M_r$	= -5.55E-01	Nm/m	
$M_t$	= -5.36E-02	Nm/m	
М	= 5.57E-01	Nm/m	
Q	= -1.16E+01	N/m	
$\sigma_{drying max}$	= 3.34E+08	N/m²	Maximum bending stress of the fluidisation load
Edrying max	= 1.71E-03	strain	Maximum strain caused by the fluidisation load

#### Strain when bed is completed drying (dried particulate)

F <sub>dryingmin</sub>	= 8.68	Ν
Adisc	= 4.05 E - 02	m²
I	= 2.66E-04	$m^4$
w	= 16.25	N/m
ν	= 0.13	
D	= 0.02	
Уь	= -4.25E-02	
$q_b$	= 9.93E-01	
$M_{ra}$	= -5.14E-01	
$Q_a$	= -9.87E+00	
Ydrying min	=-5.17E-03	m
9	= 1.21E-01	rad.
$M_r$	= -4.87E-01	Nm/m
$M_t$	= -4.70E-02	Nm/m
Μ	= 4.89E-01	Nm/m
Q	= -1.02E+01	N/m
$\sigma_{drying min}$	= 2.93E + 08	N/m²
Edrying min	= 1.50E-03	strain

The load value change mainly due to the moisture loss with time during drying producing a small strain changes. These changes estimated as the difference between the maximum and minimum load strain of the fluidised particles, which is equal to

 $y_{range} = -1.11\text{E}-02 \text{ m}$  or -11.07 mm vertical displacement  $\sigma_{range} = 4.10\text{E}+07 \text{ N/m}^2$  $\varepsilon_{range} = 2.09\text{E}-04 \text{ strain or } 209.31 \,\mu \text{strain}$ 

The Data acquisition device (DataScan 7321), has a strain sensitivity of 0.67  $\mu$  strain. Then the possible range of step changes for drying according to this calculation is dividing the range of strain by 0.67  $\mu$  strain, which are 322 steps detected for approximately 124 grams of water.

The change in the thickness of the spring disc will lead to a change in the number of steps, the thicker the disc material thickness the less number of mass change detected.

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