CASEIN DRYING

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TO TITA,

Without whose support, care and love this research work would have been far less exciting and enjoyable.

ABSTRACT

Fundamental aspects of casein drying have been investigated to provide relevant information for design, operation and control of industrial casein driers.

Casein desorption isotherms were sigmoid in shape and of type II according to the BET classification. A modified Henderson equation could describe the equilibrium moisture content (EMC) of casein as a function of water activity (equilibrium relative humidity) and temperature. Under similar drying conditions, the EMC of casein decreased in the order mineral acid > rennet > lactic. Studies on mineral acid casein indicated that the EMC was not affected by wet processing conditions but more severe drying conditions caused a significant decrease.

Drying mechanisms were studied in a laboratory tunnel drier and a fluidized bed drier. The batch drying curve in the tunnel drier consisted of a short constant rate period (CRP) and two linear falling rate periods (FRP). The critical moisture content was about 1.5 kg water/kg dry solids. In contrast the batch drying curve in the fluidized bed drier had a long constant rate period down to a critical moisture content of around 0.5 kg water/kg dry solids, followed by a single linear falling rate period.

The effects of drying conditions and casein manufacturing conditions were studied in the fluidized bed drier. The CRP drying rate was directly proportional to the air temperature driving force. The FRP drying rate also increased with an increase in air temperature. An increase in air velocity caused an increase in the CRP drying rate but did not affect the drying rate in the FRP. A rise in casein precipitation pH from 4.3 to 4.8 caused a significant reduction in the CRP drying rate but had only a small effect on the FRP drying rate. The precipitation and hot wash temperatures of casein curd had no significant effect on the drying rates. Curd plasticization did not affect the drying rate in the CRP but increased the FRP drying rate. In the CRP, larger particles (> 2.00 mm) tended to dry more slowly than smaller particles because of reduced fluidization efficiency, but particle sizes ranging from 0.50 to 3.35 mm did not appear to affect drying rates in the FRP. In general the CRP was affected by factors which altered the gas phase heat and mass transfer whereas the FRP tended to be influenced by factors affecting the solid phase heat and mass transfer.

Measurements in a commercial plant indicated that bigger casein particles leaving the drier had significantly higher moisture contents than the smaller particles. Moisture equilibration between the big and small particles was reached in about 3 hours.

Studies on drying of single casein particles indicated that lactic casein particles had higher air contents than rennet casein and mineral acid casein particles when drying from a mean initial MC of 1.2 kg water/kg dry solids to a final MC of 0.02 kg water/kg dry solids. This caused particle shrinkage of about 40% for all three types of casein which was brought about by both evaporation of moisture and contraction of the casein matrix. Below about 0.40 kg water/kg solids, the casein matrix no longer contracted significantly and the voids left by the evaporating moisture became air pores.

A pulsed NMR technique was used to obtain the self diffusion coefficient (D) and transverse relaxation time (T_2) of water in mineral acid, lactic and rennet casein particles, as well as the moisture distribution images within mineral acid casein particles. The self diffusion coefficient and transverse relaxation time for all casein types decreased with decreasing moisture content. But at the same moisture content the T_2 values for acid caseins were much higher than for rennet casein. This may be attributed to the extra mineral content of rennet casein. The maximum self diffusion coefficient of water within a casein particle was about 25% that of pure water. The T_2 of pure water was about 200 times that for acid caseins and 750 times for rennet casein. Moisture equilibration between particles took about 3 hours to reach an equilibrium D value which compares well with the value above. The proton density image within a wet casein particle showed regions of high moisture content and some regions of very low moisture content which may be air gaps.

The effects of temperature and time on casein colour and casein solubility in alkali were studied for a range of moisture contents. In general low moisture samples were more soluble than high moisture samples. However for holding temperatures up to $100^{\circ}C$ and holding time up to 2 hours, the maximum insolubility of casein occurred at a moisture content of around 0.43 kg water/kg dry solids. Casein colour was not affected by holding temperatures of up to $100^{\circ}C$ at holding times of up to one hour. However a 2 hour holding time at $100^{\circ}C$ caused severe discoloration of casein.

The implications of these results for commercial casein drying are discussed and a new design concept for casein dry processing is proposed.

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CHAPTER 1
INTRODUCTION

1.1. BACKGROUND

Historically New Zealand has been a leading exporter of casein products. In 1985 about 268,000 tonnes of casein were produced worldwide (Tinbergen, 1988). Of this, approximately 150,000 tonnes of casein entered international trade and New Zealand contributed 60,000 tonnes of this total (40%) (Southward, 1986).

Casein was first produced in the early 1900's largely for industrial uses. Over the years the casein market has slowly evolved from industrial to edible uses. Today about 80 percent of the total casein products are used for food purposes (Southward & Walker, 1982; Kirkpatrick & Walker, 1984; Tinbergen, 1988). A principal factor behind this turn around has been the recognition of the functional properties that casein can impart to food systems (Muller, 1971). These include fat emulsification, water binding, whipping and thickening as well as nutritional properties.

A number of reviews on the principles involved in the commercial production of casein have been published. Until the late 1950's casein manufacture was largely a batch operation (Dahlberg, 1939; Spellacy, 1953; Gordon, 1961). These processes were time consuming and laborious and have now been largely replaced by more efficient continuous processes (Muller, 1971). Fox (1970), King (1970), Muller (1971, 1982a & 1982b), Southward and Walker (1980 & 1982), Southward (1986) and Mulvihill (1989) have reviewed the different processing operations involved in the continuous production of casein. Figures 1.1 and 1.2 indicate the general processing steps involved in the manufacture of casein. These include the precipitation of casein from skim milk, cooking, dewheying, multiple stage washing with water, dewatering, drying, tempering, grinding and sieving, blending and bagging.

Casein drying is a very neglected area of research as shown by recent reviews in casein manufacture (Southward & Walker, 1982; Mulvihill, 1989; Mann, 1991). Most of the papers published on casein drying have extremely limited fundamental data (Bhanumurthi & Bansal, 1979; Espie *et al.*, 1984; Majkowski *et al.*, 1988).

Drying is a very important part of the casein production process, in terms of both process economics and product functionality.

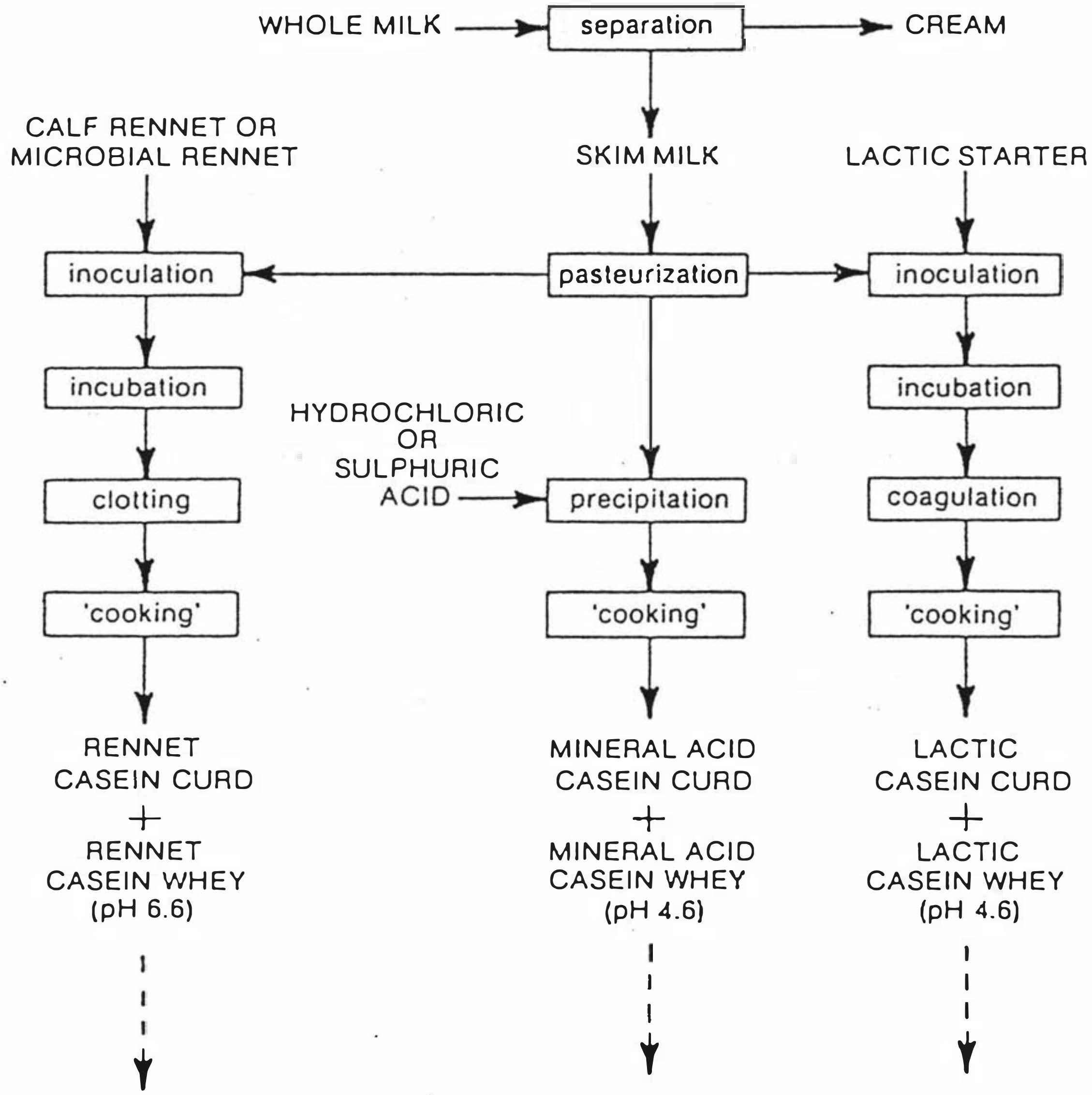


Figure 1.1. Processing steps involved in the precipitation of acid and rennet caseins from skim milk (from Southward & Walker, 1980).

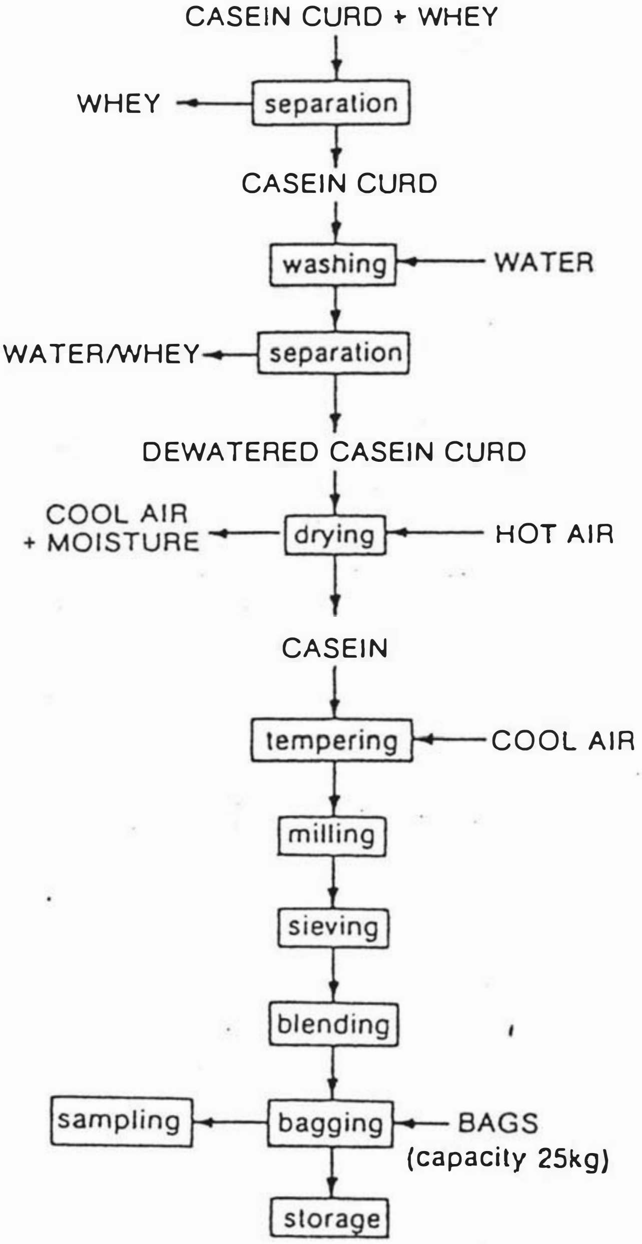


Figure 1.2. Processing steps in the washing, drying and post-drying operations of caseins (from Southward & Walker, 1980).

The current situation in New Zealand and perhaps in other casein producing countries, is that casein factories decide on the selection, operation and control of their driers with very little background fundamental data. There is therefore a need for a fundamental study of casein drying to achieve a better understanding of the drying process. The flow on benefits from such a study would include improved process control and more consistent product quality. In addition, some definite financial benefits could be expected. These are: a) reduced energy costs for drying; b) lower capital costs for new driers; c) reduced need for tempering and blending as drier control is improved; d) possibly reduced need for grinding (if this is done within the drier); and e) higher product tonnages from better drier control.

1.2. OBJECTIVES

In order to improve casein drying, the present technology needs to be updated by generating fundamental data needed in the design, operation and control of casein driers, as well as understanding the physical changes in casein brought about by the drying process.

The main objectives of the research therefore are:

a) to study the desorption characteristics of different types of casein;
b) to obtain batch drying rate curves of casein curd in two different drying regimes (the tunnel drier and fluidized bed drier);
c) to determine the effect of manufacturing and drying conditions on drying rates of casein curd;
d) to investigate the physical changes on casein during drying; and
e) to study the thermal sensitivity of casein during drying.

CHAPTER 2
LITERATURE REVIEW

2.1. CASEIN MANUFACTURE

2.1.1. Types of Casein

The two main types of casein are rennet casein and acid casein. Acid casein is further classified into mineral acid and lactic caseins. Hydrochloric and sulphuric are the most common mineral acids used in casein manufacture. In Australia and Europe, hydrochloric acid is favoured as it is a readily available and relatively cheap by-product of the chemical industry (Southward & Walker, 1982). In New Zealand, sulphuric acid is preferred because it is readily available from fertilizer works and cheaper than hydrochloric acid (Munro, 1988).

Mineral acid casein. Skim milk (pH 6.6) is pasteurized, cooled to about 25^{O}C and mixed with dilute acid (0.5 N) to achieve a pH of approximately 4.6. The acidified skim milk is heated to a temperature of 50-55^{O}C, usually by steam injection, in order to agglomerate the casein particles. Following a short residence time in a ‘cooking’ pipe and ‘acidulation’ vat, the resultant curd is separated from the whey, washed and dried (Southward & Walker, 1980).

Lactic acid casein. The skim milk is pasteurized and inoculated with defined strains of lactic acid-producing bacteria, known as ‘starter’ at a temperature of 22-28^{O}C. After a period of incubation of some 14-16 hours, during which time some of the lactose in the milk is fermented to lactic acid, the pH of the milk is reduced to about 4.6 causing coagulation of the casein. The lactic coagulum is then cooked and further processed as described for mineral acid casein (Southward & Walker, 1980).

Rennet casein. Rennet enzyme is added to skim milk typically in a ratio 1:7000 v/v at a temperature of about 29^{O}C. A clot forms after about 30 minutes at pH 6.6. The clotted milk is then cooked and the casein processed as for acid caseins, but without the acidulation step (Southward & Walker, 1980).

2.1.2. Processing Steps

Precipitation. The aggregation of casein micelles is achieved by reducing the nett negative charge on the micelles to near zero. For acid casein, this is achieved by reducing the pH to about 4.6, the isoelectric point of casein. For rennet casein, the nett negative charge is reduced by enzymic removal of the negatively charged tail from the κ-casein molecule. This action destabilizes the casein micelles which then form a three-dimensional clot with calcium ions (Munro, 1988).

Cooking. For all types of casein, precipitation occurs at a relatively low temperature in the range 20-30°C, but the coagulum or precipitate formed is soft and fragile. The cooking operation involves heating the curd to 50-55°C to cause shrinkage (or syneresis) and toughening of the curd particles. This causes whey to be released from the curd, and enables the particles to withstand mechanical handling in the washing, solid/liquid separation and drying operations (Southward & Walker, 1982).

Dewheying. After cooking, acid casein is acidulated for a few minutes prior to dewheying. This involves gentle agitation of the curd and whey to complete the solubilization of residual calcium from the acid casein curd. The curd and whey are then separated. Mechanical dewheying is usually carried out using either a horizontal solid-bowl centrifuge (Higgs *et al.*, 1973) or a roller press (Hobman & Elston, 1976) both of which are more efficient than screen dewheying.

Washing. The purpose of casein washing is to remove the water soluble constituents (whey solids) from the casein particles. This is generally carried out in a series of large horizontal D-vats using a counter-current flow of water (Southward & Walker, 1982). Typically this system requires four washes, each lasting about 15 minutes. The ratio of wash water to skim milk flowrates is generally in the range 0.5:1 to 1:1 (Southward & Walker, 1982). When the casein is to be used for food products, a hot wash of 70 to 80°C (Fox, 1970; King, 1970) is used to provide an additional pasteurization step.

Dewatering. Casein curd is mechanically dewatered to reduce the moisture content in the curd and thereby minimize the quantity of water to be evaporated in the subsequent drying step (Mulvihill, 1989). The equipment used for this operation is similar to that employed in dewheying. Mechanical dewatering by means of a horizontal solid-bowl centrifuge or a roller press should be capable of reducing the moisture content of the washed curd to within the range 52 to 56% (Southward & Walker, 1982).

Mincing and Drying. After dewatering, the curd may be minced to produce particles of uniform size and surface area for drying. Large particles or lumps tend to dry unevenly forming a hard, impervious outer surface that prevents the diffusion of the remaining moisture from the interior of the particle (Fox, 1970). Casein curd is dried to less than 12% moisture depending on the specification by contacting with hot air, typically in a vibrated fluidized bed drier or a pneumatic conveying drier (Neff, 1966a & 1966b; King, 1970).

Tempering. Casein is tempered for periods of up to 24 hours to equilibrate the moisture content both within and between casein particles. Tempering also cools and hardens the casein so that it can be ground effectively (Fox, 1970; King, 1970). Typically the dried casein is withdrawn from the bottom of a bin and pneumatically conveyed into another bin. This has the advantage that the air used for transport of the casein assists in cooling the particles. Insufficient tempering can cause the large moist particles to adhere to the rolls during milling with consequent processing delays (Southward & Walker, 1982).

Milling and Sieving. These two operations are most conveniently considered together since they are usually combined in a size reduction/size separation circuit. Roller mills are commonly used for grinding casein and in New Zealand, pin mills are also employed when finer casein is required. Casein is sieved into different size fractions using vibrating sifters. These consist of a stack of flat screens mounted on a frame which is driven with a gyratory motion. Occasionally, rotary screens are used (Southward & Walker, 1982).

Blending. After sifting the casein is blended to ensure uniform quality throughout the batch. Blending is carried out by means of a bin transfer system (King & Jebson, 1970; Jebson, 1972).

2.1.3. Casein Drying

The casein curd is dried to a product with 10 to 12% (w.b.) moisture before packaging. There are economic advantages in achieving a final moisture as close as possible to the required specification. However after leaving the drier the casein can continue to lose moisture depending on the casein exit temperature, the amount of air conveying used, and the air humidity (Morison *et al.*, 1990). Typical reductions in moisture content are 1.5% (w.b.) during cooling and tempering, and 1% (w.b.) during grinding. Curd should therefore leave the drier at 13 to 14% (w.b.) moisture (Munro, 1988).

Casein is a protein with a very loose and flexible tertiary structure and hence it is not as sensitive to heat denaturation as most other proteins. Many casein driers therefore use countercurrent flow whereby the hottest air contacts the driest curd and operate without significant casein denaturation and insolubilization (Munro, 1988). Air inlet temperatures of up to 145°C are often used for fluidized bed driers (Arapov *et al.*, 1984; Majkowski *et al.*, 1988).

A number of different types of drier have been used for casein drying. The four common types are:

a) vibrated bed drier (NDA, Pillet);
b) fluidized bed drier (Niro);
c) pneumatic conveying drier or ring drier (Berk, Barr & Murphy); and
d) attrition drier (Procalex).

Vibrated bed drier. This is the most common type of casein drier in New Zealand. The NDA drier is a modification of the Bates drier and is totally enclosed. The casein is vibrated along horizontal perforated plates. Hot air flows up through the decks countercurrent to the casein flow. There are two separate drying stages, consisting of a 2 deck predrier and a 4 deck final drier. The fines in the exhaust air are removed by a cyclone and casein falling through the screens is removed by pneumatic conveyor. The Pillet drier is a single stage 2 deck drier. It is also fully enclosed and has a thermally efficient design in which secondary air at about $140^{o}C$ is injected between the two decks to increase the temperature of air reaching the top deck. The casein curd is also cooled internally before leaving the drier (Munro, 1988).

Fluidized bed drier. The Niro drier is a single fluidized bed drier in which the casein is fluidized by the passage of hot air passing up through the bed. The bed is vibrated to prevent channeling of air through the casein and loss of fluidization. It is a large capacity drier but it is difficult to start up (Munro, 1988).

Ring drier. The ring drier (Berk, Barr & Murphy) consists essentially of a duct in the shape of a ring in which heated air and casein particles are circulated co-currently. An in-line hammer mill ensures the largest particles are broken down within the drier. The residence time of the product is controlled by centrifugal classification in the manifold. Here the drying air is renewed. The lightest and finest fractions of casein (which dry more quickly) are passed with the spent air into a cyclone, whereas the coarser and wetter fractions are held in circulation to be further dried and size reduced (Barr & Barr, 1975).

Attrition drier. The Procalex drier features a fast-revolving (1800-2000 rpm) multi-chambered rotor and a stator with a serrated surface. The curd particles are pulverized to a very small size and simultaneously dried in an air stream which passes through the drier co-currently with the product. Drying occurs at an extremely fast rate due to the large surface area created and gives a product similar to ground spray-dried casein.

The dried casein leaves the drier at a temperature of 80 to 90^{o}C (Roeper, 1982).

Most of the published papers on casein drying have very limited fundamental data useful for design and control of casein driers. In 1968 Patchett reported the energy requirements for a number of vibrated bed driers. Bhanumurthi and Bansal (1979) reported the drying of casein with different bed depths in a through circulation drier. The drying characteristics of a number of pilot plant casein curd types have been determined in a laboratory-scale fluidized bed drier (Espie *et al.*, 1984). Majkowski *et al.* (1988) published results on fluidized bed drying of casein using a distributor plate with multi-whirl flow.

Casein is a biologically derived material which would have some similarities with other biological products. Since studies on casein drying are very limited it is necessary to review the literature on drying of biological materials. Knowledge gained from this review should give some ideas applicable to casein drying.

2.2. DRYING OF BIOLOGICAL MATERIALS

2.2.1. Background

Drying or dehydration is defined as the removal of moisture from a material through vaporization or sublimation (in the case of freeze drying) (Karel, 1975; Watson & Harper, 1988). There are a number of reasons for drying biological materials such as foodstuffs, the most important of which is extension of shelf life. Drying achieves this by reducing the moisture content of the product to levels which inhibit microbial growth and which significantly reduce other deleterious reactions. Aside from preservation, drying reduces the product weight and volume which decreases transportation and storage costs, and provides convenience for consumers.

Haertling (1980) pointed out that the design of driers requires knowledge of the drying rate as a function of moisture content at constant drying conditions. As it is impossible to predict drying rates from heat and mass transfer theories alone, the drying rates must be obtained experimentally. In actual drying operations, determining the effect of variables on drying is complicated because of feed fluctuations, complicated air flows, changing air temperature and humidity conditions and others. Measurements of the batch drying rates of the material at constant conditions are better suited for this purpose. Theory can be used to convert data obtained under one set of conditions to another. The basis of drier designs is measurements of batch drying data using conditions as close as possible to the actual process. Batch drying data can also be converted to continuous drying using plug flow driers.

Batch drying experiments involve monitoring moisture content (M) with time (t) under controlled conditions (Figure 2.1a). The moisture content of the material is usually expressed on a dry basis (kg water/kg dry solids). There is usually a short initial settling down period as the surface heats up to the wet bulb temperature (stage AB). After the transition period, the curve is straight and relatively steep, indicating a rapid rate of drying while the moisture content is high (stage BC). As the moisture content drops the curve becomes less steep and finally approaches the equilibrium moisture content asymptotically (stage CD).

The slope of a tangent to the drying curve (dM/dt) represents the drying rate of the sample at a particular moisture content or time. Taking the slopes over the entire curve, plots of drying rate against moisture content or time are obtained (Figures 2.1b and 2.1c, respectively). Since drying rate is intrinsically related to moisture content rather than time, Figure 2.1b rather than Figure 2.1c is the appropriate method of representing the fundamental behaviour of the sample (Karel, 1975; Brennan *et al.*, 1976; Watson & Harper, 1988). Stage BC is known as the constant rate period of drying whereas stage CD is called the falling rate period of drying. Where the constant rate period ends and the falling rate period begins is called the critical moisture content. This corresponds to the moisture content (M_c) when Point C is projected on the x-axis. Point D represents the equilibrium moisture content (M_e) of the product under the given drying conditions.

2.2.2. Fundamentals of Drying

Constant Rate Period. During the constant rate period (CRP) the surface of the material remains saturated with liquid water, because the movement of the moisture within the solid to the surface takes place at a rate equal to the rate of evaporation from the surface. Drying takes place by movement of water vapour from the saturated surface through a stagnant air boundary layer into the main stream of the drying air. The rate of drying is dependent on the rate of heat transfer to the drying surface. The heat required to evaporate the water exactly balances the rate of heat transfer from the drying air to the drying surface. The temperature of the drying surface therefore remains constant and corresponds to the wet bulb temperature of the drying air (Brennan *et al.*, 1976).

The temperature driving force from the air to the solid is the difference between the dry and wet bulb temperatures, which remains constant during this period. The

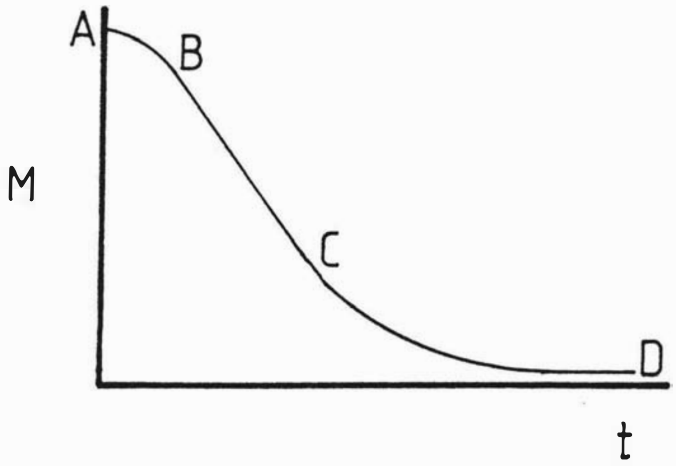


Figure 2.1a. Drying curve of a biological material.

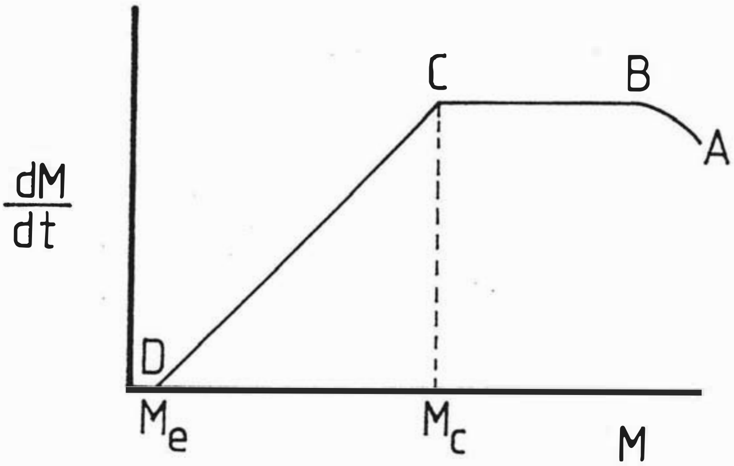


Figure 2.1b. Drying rate curve of a biological material (moisture content plot).

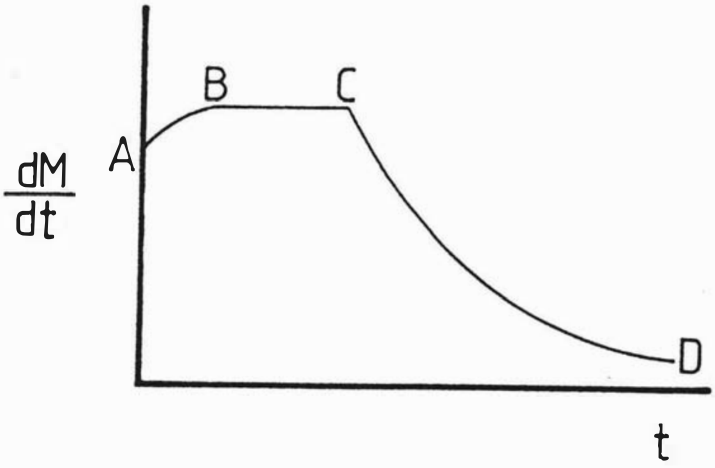


Figure 2.1c. Drying rate curve of a biological material (time plot).

humidity driving force causes the diffusion of vapour through the stagnant air film and into the main stream of the drying air. The relationship governing this period is,

$$R_c = \frac{(dM/dt)_c \, W}{A} = \frac{h\,(T_a - T_w)}{L} = k_m\,(H_w - H_a) \qquad (2.1)$$

where: R_c = constant evaporation rate (kg water/m^2*second)
$(dM/dt)_c$ = CRP drying rate (kg water/kg dry solids*second)
W = mass of dry solid (kg)
A = available drying area (m^2)
h = heat transfer coefficient (W/m$^{2\,o}$C)
$(T_a - T_w)$ = temperature driving force (^{o}C)
T_a = dry bulb temperature of the drying air (^{o}C)
T_w = wet bulb temperature of the drying air (^{o}C)
L = latent heat of vaporization of water (J/kg)
k_m = mass transfer coefficient (kg dry air/m^2*second)
$(H_w - H_a)$ = humidity driving force (kg water/kg dry air)
H_w = humidity ratio of the air at T_w (kg water/kg DA)
H_a = humidity ratio of the air at T_a (kg water/kg DA)

When the temperature and humidity driving forces change appreciably between the inlet and outlet, then the log mean driving forces for mass and heat transfer must be used (Nonhebel & Moss, 1971),

The rate controlling factors during the CRP are therefore: a) the available drying area; b) the temperature or humidity driving forces; and c) the heat or mass transfer coefficients.

Brennan *et al.* (1976) mentioned that in estimating the CRP drying rate, the use of heat transfer coefficients is more reliable than mass transfer coefficients. The heat transfer coefficient is related to mass flow rate of air using the following equations:

For parallel air flow, $h = 14.3\,G^{0.8}$ $(\mathrm{W/m^{2\,o}C})$ (2.2)

For perpendicular air flow, $h = 24.2\,G^{0.37}$ $(\mathrm{W/m^{2\,o}C})$ (2.3)

where: G = mass flow rate of air (kg/m^2*second)

The mass transfer coefficient can be calculated from the Lewis relationship with the heat transfer coefficient,

$$Le = h/(k_m C_s) \tag{2.4}$$

where: Le = Lewis number

C_s = humid heat of the drying air (J/kg DA ^oC)

For the air/water system the Lewis number is approximately unity (Watson & Harper, 1988).

The CRP drying rate can be determined from the initial moisture content (M_o), the critical moisture content and the duration between these two moisture levels (t_c),

$$(dM/dt)_c = \frac{(M_o - M_c)}{t_c} \tag{2.5}$$

Falling Rate Period. As drying proceeds, a point is reached where the rate of movement of moisture within the material to the surface is reduced to the extent that the surface begins to dry out and the rate of drying begins to fall. The surface temperature of the material begins to rise and continues to do so as drying proceeds, approaching the dry bulb temperature of the air. Some products may exhibit more than one FRP (Brennan *et al.*, 1976).

There appear to be four major modes of moisture movement within solid materials: a) liquid movement by capillary forces; b) liquid diffusion due to concentration gradients; c) vapour diffusion due to partial pressure gradients; and d) diffusion in liquid layers adsorbed at solid interfaces (Charm, 1978; Van Arsdel *et al.*, 1973). Brennan *et al.* (1976) observed that the mechanisms of capillarity and liquid diffusion have received the most detailed treatment. In general, capillarity is most applicable to coarse granular materials, and liquid diffusion to single phase solids with colloidal or gel like structures. In many cases it appears that the two mechanisms may be applicable to a single drying operation, i.e. capillarity accounting for the moisture movement in the early stages of drying while a diffusional mechanism applies at lower moisture contents.

For the case of a single linear FRP, the line can be represented by the equation,

$$(dM/dt)_f = F\,(M - M_e) \tag{2.6}$$

where:

$(dM/dt)_f$ = FRP drying rate at time, t (kg water/kg DS*second)
F = FRP drying coefficient (1/second)
M = average moisture content of the material at time, t (kg water/kg dry solids)
M_e = equilibrium moisture content of the material at the given drying conditions (kg water/kg dry solids)

The above equation is called the exponential or logarithmic model (Henderson, 1974). The FRP drying coefficient represents the combined effect of all the mass transfer mechanisms and cannot reliably be interpreted in terms of a specific diffusivity (Watson & Harper, 1988).

For linear FRP, knowing the CRP drying rate, the critical moisture content (M_c) and the equilibrium moisture content (M_e), the FRP drying coefficient can be calculated,

$$F = \frac{(dM/dt)_c}{(M_c - M_e)} \tag{2.7}$$

Henderson and Pabis (1961) have shown the theoretical justification for using an Arrhenius type equation to relate the FRP drying coefficient to temperature. Several investigators have reported that the FRP drying coefficient is a function of the absolute temperature for a variety of biological materials (Ross & White, 1972; White *et al.*, 1981; Chiang & Petersen, 1985; Verma *et al.*, 1985; Ajibola, 1989).

Most investigators dealing with drying of biological materials with definite dimensions such as slabs and spheres describe drying in the falling rate period using the Fick's diffusion equation (Jason, 1958; Suarez *et al.*, 1980; Chirife, 1983). This model predicts that the rate of drying in the FRP is inversely related to the square of the material thickness. For materials in which moisture movement is controlled by capillary flow, the FRP drying rate is inversely related to the sample thickness (Brennan *et al.*, 1976). These models suggest that the particle size of the material is an important factor during the FRP regardless of the mechanism of moisture movement.

2.2.3. Hot Air Drying Studies

A wide variety of driers have evolved over the years for drying different materials. Several methods have been suggested to classify these driers (Forrest, 1968; Williams-Gardner, 1971; Karel, 1975; Brennan *et al.*, 1976; Dittman, 1977).

Driers may be classified into: a) convection driers; b) conduction driers; and c) radiation driers. Drying may be either batch or continuous, and can be carried out under vacuum or atmospheric pressure.

Examples of convection driers are: a) kiln driers; b) tray or cabinet driers; c) tunnel driers; d) bin driers; e) fluid bed driers; f) spray driers; g) pneumatic or ring driers; and h) rotary driers. Convection driers a) to d) are called fixed tray driers. Examples of conduction driers are: a) drum driers; b) vacuum shelf driers; c) vacuum double cone driers; d) trough driers; and e) pan driers. An infra-red drier is an example of a radiation drier (Williams-Gardner, 1971; Brennan *et al.*, 1976).

Convection or hot air driers are the most common driers for handling solid materials because of their versatility and ease of operation. Fixed tray drying and fluidized bed drying of biological materials will be considered specifically since they are more relevant to casein drying.

Fixed Tray Drying. Fixed tray driers are the most common type of drier. They are easy to operate and have lower capital costs than many other types of drier. Hence most drying studies on biological materials have been carried out in fixed tray driers, such as the tunnel drier.

Early studies on drying fruits and vegetables indicated the presence of constant rate periods for many samples (Saravacos & Charm, 1962). However later studies reported no constant rate period for most biological materials. Bimbenet *et al.* (1985) published a review on the fixed tray air drying of biological materials and found that most materials did not have a constant rate period but instead had two falling rate periods. The main determining factor appeared to be the type of product. In many cases there was an Arrhenius-type of relationship between air temperature and drying rate. Air humidity and velocity tended to have a significant effect at the beginning of drying but the effect later on in drying was dependent on the product being dried. Particle size also had a strong influence. They concluded that no theory could presently predict the drying kinetics of biological materials. A review by Chirife (1983) also reported the absence of a CRP and the presence of more than one FRP in foodstuffs.

Jason (1958) reported the presence of a CRP and two FRP's in drying fish muscle. He reported that the CRP drying rate was controlled by ambient conditions and was equal to that from a saturated surface of the same shape. Drying during the FRP took place in two distinct phases, in each of which the behaviour was in accord with a solution of the diffusion equation based on Fick's Law. Both coefficients varied with temperature according to an Arrhenius type equation.

Salas and Labuza (1968) published drying rate curves of model food systems. These authors found that the drying of these samples consisted of a CRP and two FRP's. However the two stages of the FRP could actually be approximated by a single line.

Keey (1964) reported the drying characteristics of rewetted sodium caseinate in a fixed tray drier. He observed the presence of a CRP and two FRP's. A critical moisture content of 0.24 kg water/kg dry solids was found using a drying temperature of 71^{O}C.

Fluidized Bed Drying. Fluidized bed driers are extensively used in the chemical, food, mining, pharmaceutical and plastics industries for thermal drying of a wide spectrum of granular solids (Gupta & Mujumdar, 1983). Danielsen and Hovmand (1980) mentioned that the principal advantages of fluidized bed driers are good solids mixing and the large surface area available for heat and mass transfer as compared with fixed tray driers. They also pointed out that by using vibrated fluid beds, materials can be dried that are often difficult to fluidize. Factors which make some materials difficult to fluidize are:

a) a wide particle size distribution;
b) low particle strength;
c) stickiness or thermoplasticity; and
d) pasty properties of the wet feed.

Mazza and Le Maguer (1980) reported drying onions in a vibro fluidizer at different temperatures. They found that there was a short CRP when drying onions at 40^{O}C but as the temperature increased to 50 and 65^{O}C the CRP disappeared. They also observed the presence of two FRP's at all temperatures.

Le Maguer and Mazza (1984) also studied the drying characteristics of carrots in a vibro fluidizer at different air temperatures and flow rates and under various loading ratios. They reported that drying of carrots occurred in the FRP only. They also found that the heat transfer coefficient and surface diffusivity for carrots decreased with moisture content.

The gas-particle heat transfer coefficient in fluidized pea beds at different air flows and bed heights have been reported (Vazquez and Calvelo (1980). The authors found that bed height of peas during fluidization had no effect on the heat transfer coefficient, but there was a slight dependence of the heat transfer coefficient on the superficial air velocity.

John *et al.* (1990) investigated the fluidized bed drying of bread and biscuit crumbs and obtained the particle size distribution, fluidization behaviour and drying kinetics for all the products. The samples had a wide particle size distribution from 0.5 to 5.0 mm and an average d_{50} of 2.5 mm and were successfully fluidized in a conical shaped bed. The crumbs studied differed considerably in their fluidization behaviour. The average critical moisture content was 0.3 kg water/kg dry solids and all samples exhibited a short CRP and more than one FRP.

2.2.4. Sorption Isotherms

The moisture contained in a food product exerts a vapour pressure which is dependent on the nature of the moisture, the nature of the solid and the temperature. When the product is exposed to an environment of fixed partial vapour pressure, it will either lose (desorb) or gain (adsorb) moisture until the vapour pressure of the moisture in the product equals the vapour pressure of the surroundings.The moisture content of the product at this point is known as the equilibrium moisture content (EMC).

A graphical relationship between the EMC of a material and its equilibrium relative humidity (ERH) at constant temperature is termed the equilibrium moisture curve (Henderson, 1952) or sorption isotherm (Labuza, 1968). The most popular way of reporting sorption isotherms is a plot of EMC against the decimal form of ERH, also known as water activity (a_w).

Foods are complex materials which give rise to desorption isotherms that are usually higher than adsorption isotherms. This phenomenon is due to hysteresis (Labuza, 1968). Kapsalis (1987) reviewed different theories proposed for sorption hysteresis which included: a) the incomplete wetting theory; b) the ink bottle neck theory; c) the open-pore theory; and d) the domain theory.

The sorption isotherm is a very important characteristic of foods, since it influences several aspects of drying and storage. Sorption isotherms of foods constitute an essential part of the theory of drying (King, 1968), are important for the accurate design of drying equipment, particularly near the end of drying (Iglesias *et al.*, 1975), and can contribute to an understanding of the kinetics and mechanism of drying (Loncin *et al.*, 1968). Sorption isotherms can also distinguish between the bound and unbound moisture of foods. Bound moisture is defined as that moisture which exerts a lower vapour pressure than that of pure water at the same temperature, while unbound moisture has a vapour pressure equal to that of water (Williams-Gardner, 1971; Watson & Harper, 1988). Hence bound moisture is the moisture of the product when a_w is less than 1.

In drying operations, desorption isotherms of foods at different temperatures are needed for the EMC determination of the material at the given relative humidity and temperature existing inside the drier. The EMC of the product is the lowest moisture content that can be achieved under a given set of drying conditions (Brennan *et al.*, 1976; Watson & Harper, 1988). The difference between the total moisture and the EMC represents the amount that can be removed by drying and is called the free moisture content. This may include both bound and unbound moisture (Williams-Gardner, 1971; Watson & Harper, 1988).

There are a number of methods for obtaining sorption isotherms which include: a) gravimetric (Gal, 1981); b) manometric (Iglesias & Chirife, 1982); c) hygrometric (Iglesias & Chirife, 1982); and d) dynamic (Hustrulid & Flikke, 1959; Henderson, 1974). EMCs obtained from the dynamic method are usually higher than those obtained using the static methods (a, b & c), presumably because the measured values were observed under moving or dynamic conditions (Henderson, 1974).

Sorption Isotherm Equations. Equations that can describe the sorption isotherms of foods are of special interest in the prediction of drying times (King, 1968) and the prediction of the shelf life of packaged dried products (Karel *et al.*, 1971; Labuza *et al.*, 1972). The isotherm equation is also needed for evaluating thermodynamic functions for the water absorbed in foods (Iglesias *et al.*, 1976).

A number of theoretical models which have been derived from the physical chemistry of surfaces, have been used to fit the observed sorption isotherms (Chirife & Iglesias, 1978).

The usefulness of a sorption equation will depend on the desired objectives of the user. For instance, in the prediction of drying times or the shelf life of packaged food, the user is interested in an equation which fits as closely as possible to the experimental data and perhaps is less concerned with the theoretical basis for the equation (Labuza, 1968). The number of parameters required in the equation is another important factor, particularly for the mathematical simulation of the drying process (Boquet *et al.*, 1978).

Chirife and Iglesias (1978) have reviewed twenty three equations which have been reported in the literature for fitting sorption isotherms of foods, thirteen of which are two-parameter equations. Boquet *et al.* (1978) evaluated the various two-parameter models for fitting water sorption isotherms of foods. They found that the Oswin equation gave the best fit for sorption isotherms of proteins, followed by the Henderson and the Bradley equations.

All two-parameter isotherm equations mentioned above are only applicable at the specific temperature at which the parameters were derived. It is therefore necessary to derive an equation which takes into account the effect of temperature on the sorption isotherms. Several investigators have reported equations that describe the temperature dependency of sorption isotherms of foods with varying success (Day & Nelson, 1965; Chen & Clayton, 1971; Iglesias & Chirife, 1976a; Putranon *et al.*, 1979; Diamante & Munro, 1990).

2.2.5. Physical Changes During Drying

During drying of biological materials, physical and structural changes accompany the loss of moisture (Karel, 1975; Brennan *et al.*, 1976). Particle shrinkage is one of the important physical changes that occur during drying. Drying calculations usually assume that the material being dried maintains a constant shape and no shrinkage occurs. In practice this is not the case (Charm, 1978). Shrinkage of particles also affects bulk density which is important in packaging.

Gorling (1958) suggested that the reason the drying rate is not constant in certain materials, is because the surface area is changing as moisture is removed. Kilpatrick *et al.* (1955) pointed out that, during the early stages of drying, the shrinkage in volume of vegetable pieces equals the volume of water lost by evaporation, but as the moisture content falls, any further volume shrinkage is gradually reduced. When the moisture content falls below 20% (w.b.) there is no longer a significant decrease in volume. Suzuki *et al.* (1976) measured shrinkage in terms of surface area using photography in dehydration of carrots, potatoes, sweet potatoes and radishes. They found that the surface area of potato and sweet potato shrunk to about half of the original area when the moisture content was reduced to about 33% (w.b.). If this area shrinkage is converted to volume shrinkage the values would be lower than 50%, e.g. 37% of the original volume for potato (see Appendix 2.1 for calculations). Lozano *et al.* (1983) reported that in drying different types of vegetables, volume shrinkage decreases with moisture content. Their results also suggest that the higher the initial moisture the greater the overall shrinkage of the material. The final volume of the bone dry samples were approximately: a) 30% of the original volume for sweet potato and garlic (average initial moisture was 2.4 kg water/kg dry solids); b) 20% for potato (4.5 kg water/kg dry solids); and 10% for carrot and pear (7.3 kg water/kg dry solids).

In drying casein curd, the particles may not only shrink due to loss of moisture but also due to syneresis, which is temperature dependent (O'Meara & Munro, 1982).

CHAPTER 3
EXPERIMENTAL

3.1. MATERIALS

3.1.1. Laboratory Casein

Reconstituted Skim Milk. Tap water was heated to about 45°C in a steam jacketed vessel (10 litre capacity). Low heat skim milk powder (N.Z. Cooperative Dairy Co., Ltd.) was mixed in to produce skim milk with a total solids content of approximately 9% w/w. The mixture was stirred gently using a stainless steel spoon until all the powder dissolved completely. Low heat skim milk powder was used since there is little denaturation of the whey proteins and hence it approximates fresh skim milk.

Studies have shown that the composition of fresh milk changes significantly throughout the year (Newstead *et al.*, 1976 & 1977). Therefore to ensure that a constant milk composition could be maintained in all experiments milk reconstituted from low heat skim milk powder was used. All the laboratory made casein curd used in the experiments was produced from reconstituted skim milk.

Mineral Acid Casein. The reconstituted skim milk was heated to 53±1°C in a steam jacketed vessel. Dilute (0.3 M) sulphuric acid (Analar grade; BDH Chemicals Ltd., England) was rapidly mixed into the skim milk to obtain the desired whey pH. The precipitation pH of the casein curd samples was varied between 4.0 and 5.0. Samples with precipitation pH of 4.55 to 4.65 were considered to be the standard samples. The curd/whey was stirred gently for 10 minutes using a stainless steel spoon. After 10 minutes, a small whey sample was taken and cooled to room temperature for pH determination. A Radiometer PHM82 pH meter with a Radiometer GK2401C electrode was used in the determination.

The mixture was drained on a stainless steel mesh screen (0.7 mm) for 8 minutes to separate curd and whey. The curd was given three 10-minute washes with tap water at temperatures of 55±1°C, 75±1°C and 35±1°C, respectively. The curd was stirred gently for the duration of each wash. The curd and wash water was drained on a stainless steel mesh screen (0.7 mm) for 8 minutes after each wash. The big lumps of curd were broken into smaller particles by passing through a noodle maker (width of gaps in rollers = 5 mm).

Lactic Casein. Reconstituted skim milk was cooled down to 30±1°C and inoculated with 1.25% gas producer mixed starter culture (Espie *et al.*, 1984) courtesy of the New Zealand Dairy Research Institute (NZDRI). The mixture was stirred gently to ensure even starter distribution. The inoculated milk was incubated for about 23 hours in a 30°C water bath, in order to attain a coagulum pH of about 4.6. The coagulated milk was heated slowly to 53±1°C in a steam jacketed vessel with gentle stirring. The procedure was then the same as for mineral acid casein.

Rennet Casein. Reconstituted skim milk was cooled down to 30±1°C and inoculated with calf rennet in the proportion of 1:4500 v/v. The mixture was vigorously stirred for 30 seconds and then left to stand until the milk had coagulated (30-50 minutes). The coagulated milk was cooked by heating slowly to 51±1°C with gentle stirring. The procedure was then the same as for mineral acid casein except that four washes at 40±1, 55±1, 75±1 and 35±1°C, respectively were used.

3.1.2. Pilot Plant Casein

Mineral acid, lactic and rennet casein curd were obtained from the NZDRI pilot plant for fluidized bed drying and thermal sensitivity experiments. The standard manufacturing procedure was as described by Jablonka and Munro (1986a) but with the following amendments. The precipitation temperature used was 50°C and the curd was dewatered in a Conturbex worm/screw centrifuge at 30±2°C. The precipitation pH of the mineral acid casein dewatered in the Conturbex was between 4.55-4.65.

To investigate the effect of precipitation pH and dewatering conditions on drying for mineral acid casein, variations to standard conditions were made. Casein curd was precipitated at pH of 4.3, 4.6 and 4.8. An Alfa Laval decanter was used for dewatering using temperatures ranging from 24 to 58°C.

The casein curd which was not immediately used was stored in a cool store (1-3°C) for no longer than one week.

3.1.3. Commercial Casein

Lactic casein curd was obtained from the Tui Milk Products casein factory at Longburn, Palmerston North for the fluidised bed drying experiments. The manufacturing steps were similar to that described by Southward and Walker (1980) but the casein curd was dewatered in a Conturbex centrifuge at 35±2°C. The samples were stored at about 2°C until use (usually less than one week).

3.2. EQUIPMENT

3.2.1. Tunnel Drier

The laboratory tunnel drier (Figure 3.1) consisted of a centrifugal fan, a plenum chamber and a drying chamber. A variable speed centrifugal fan was used to control the air velocity ($\pm$0.1 m/s). The air was heated with a steam heat exchanger and a series of on/off 1 kW heating elements to provide the base heat load. A proportional controller connected to 2 heating elements provided temperature control ($\pm 1^{\circ}$C). To ensure fully developed flow and to reduce swirl there were several meters of ducting with flow straighteners between the plenum and drying chambers. A stainless steel mesh drying tray (0.17 m x 0.17 m) was suspended from a weighing system in the drying chamber. The weighing system consisted of an electronic digital balance (Mettler PE 1600, Switzerland) connected to an IBM compatible personal computer (Redstone XT Computer, Taiwan), which was used to monitor the mass loss of the sample over the drying period.

3.2.2. Fluidized Bed Drier

The laboratory fluidized bed drier (Figures 3.2 and 3.3) consisted of a Rootes blower, a plenum chamber and a drying chamber. The Rootes blower (Wade Engineering Ltd., England) was linked to a frequency modulator (PDL Electronics Ltd., New Zealand) for the control of air velocity ($\pm$0.1 m/s). Air velocity was measured with a standard orifice plate (BS 1042, 1981) and a water manometer. There was a calming length of 9 pipe diameters upstream of the orifice plate and 5 pipe diameters downstream. The air was heated with a steam heat exchanger and a series of on/off 1 kW heating elements to provide the base heat load. A one kW element on a rheostat and two 1 kw elements connected to a proportional controller provided temperature control ($\pm 1^{\circ}$C). Two sets of flow straighteners were installed below the drying chamber to ensure fully developed flow and to reduce swirl. The drying chamber consisted of a stainless steel cylinder (0.245 m inside diameter) with an air distributor plate (5.8% open area). The distributor plate could be vibrated (4 mm amplitude) using a small motor, and the frequency could be varied independently. Casein samples (8-10 g) were rapidly taken using a sampling device at the base of the fluidized bed drier. Figure 3.4 shows a close up view of the drying casein and the sampler in operation. A filter bag was used to retain the fine casein particles in the drier. The inlet and outlet air temperatures were measured with fine wire thermocouples connected to a temperature recorder (Molytek, USA).

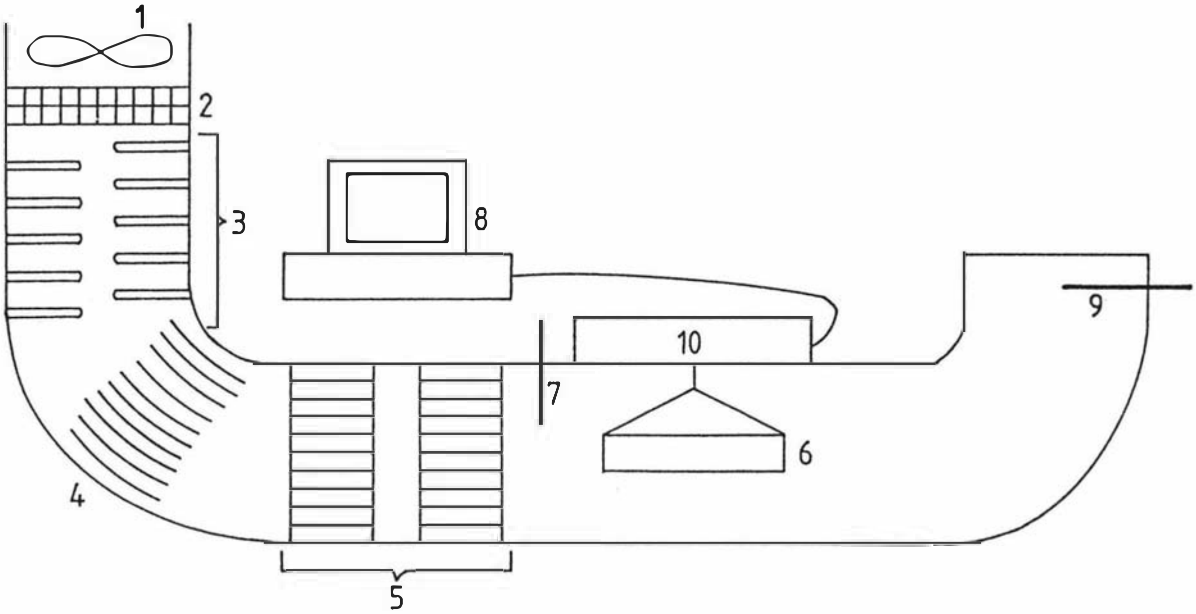


Figure 3.1. Schematic drawing of the tunnel drier showing centrifugal fan (1), steam heater (2), electrical heaters (3), straightening vanes (4), flow straighteners (5), drying tray (6), inlet air thermometer (7), personal computer (8), outlet air thermometer (9) and weighing balance (10).

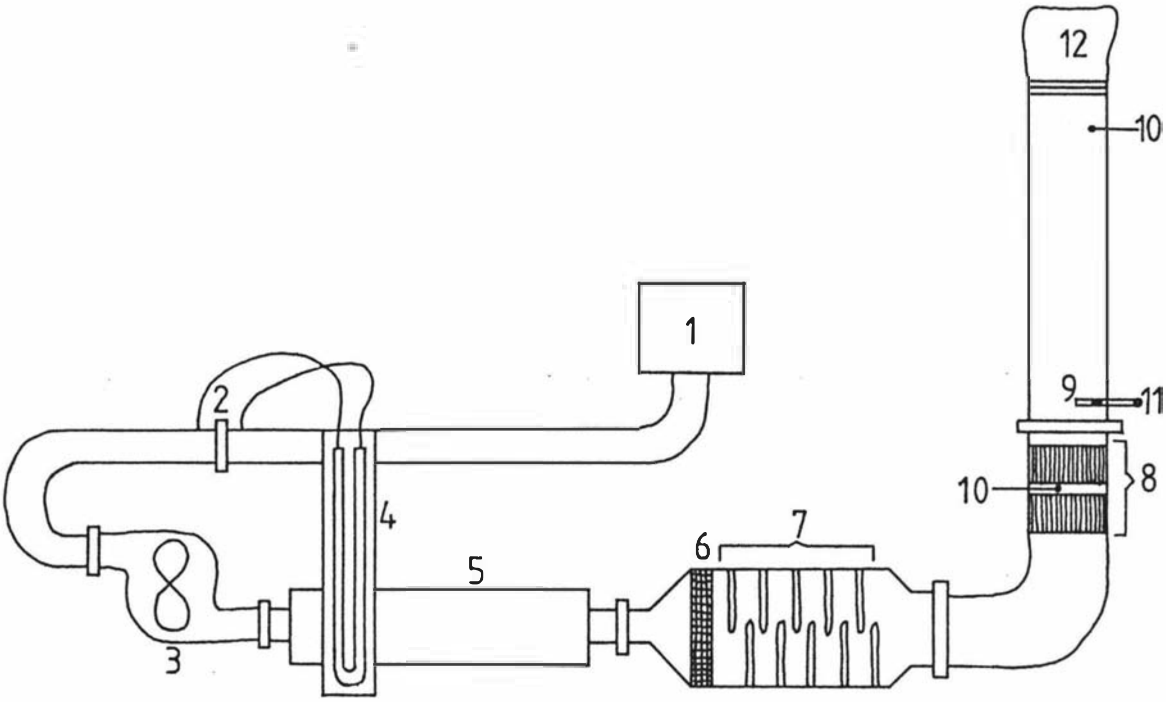


Figure 3.2. Schematic drawing of the fluidized bed drier showing air filter (1), orifice plate (2), rootes blower (3), water manometer (4), blower silencer (5), steam heater (6), electrical heaters (7), flow straighteners (8), drying chamber (9), thermocouples (10), sampling device (11) and filter bag (12).

Figure 3.3. The fluidized bed drier in operation.

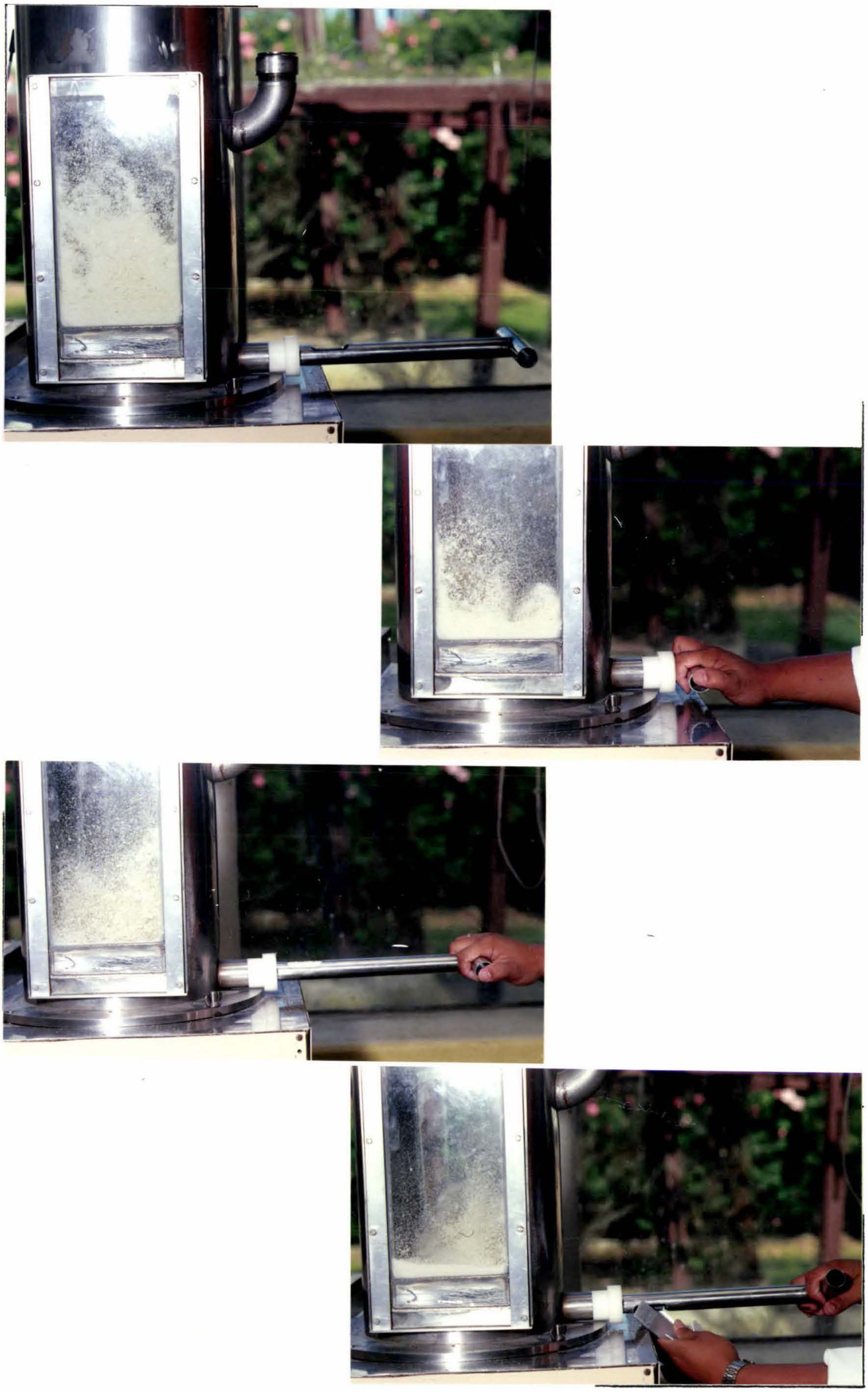


Figure 3.4. A close up view of the drying casein and the sampler in operation.

3.2.3. Nuclear Magnetic Resonance Apparatus

All Pulsed Gradient Spin Echo (PGSE) and imaging Nuclear Magnetic Resonance (NMR) experiments were performed at approximately 30°C using a modified computer controlled JEOL FX60 spectrometer (Callaghan *et al.*, 1980, Eccles and Callaghan, 1987). PGSE experiments were carried out using a specially constructed high gradient probe which could generate gradients of around 1.18 Tesla $m^{-1}A^{-1}$. Gradients of up to 12 Tesla m^{-1} were needed to produce very short pulse separation times as T_2 values as short as 1.5 ms were encountered. A separate imaging probe was used for the NMR imaging experiments. This incorporated quadrupolar G_x and G_z gradient coils of 0.24 Tesla $m^{-1}A^{-1}$ and 0.15 Tesla $m^{-1}A^{-1}$, respectively. A 0.094 Tesla $m^{-1}A^{-1}$ planar G_y coil was used for slice selection and velocity and diffusion contrasting.

3.3. METHODS

3.3.1. Casein Desorption Isotherms

3.3.1.1. Equilibration of Casein Samples

A proximity equilibration cell described by Lang *et al.* (1981) was used in the determination of desorption isotherms. However, stainless mesh was used instead of filter paper to suspend the sample over the salt solution. The use of filter paper was abandoned because it was not strong enough to hold the wet curd sample. Sixty three plastic containers were prepared with saturated salt solutions to give a range of relative humidities at different temperatures using the data of Greenspan (1977).

A 5 g curd sample was suspended in each container and placed in a constant temperature cabinet (±0.5°C). Once a week a sample was taken out of the container, weighed and then replaced. This took less than 1 minute. A Mettler AE160 balance (Mettler Instruments Ltd., Switzerland) with an accuracy of 0.1 mg was used for all weighings. When 3 consecutive weekly readings differed by less than 1 mg, the equilibrium moisture content was considered to be reached.

3.3.1.2. EMC Determination

After equilibration the samples were weighed and transferred to an aluminium moisture dish and dried in a vacuum oven (Townson and Mercer Ltd., England) for 24 hours at 70°C and vacuum pressure of 750 mm Hg (Hardy & Steinberg, 1984). The samples were then placed in a 105±1°C air oven (Clayson Laboratory Apparatus Ltd., New Zealand) for 5 hours to evaporate any remaining traces of moisture. The dried samples were cooled in a dessicator with silica gel before weighing. The EMCs were calculated on a dry basis (kg water/kg dry solids).

3.3.2. Tunnel Drying of Casein Curd

3.3.2.1. Rapid Method of Moisture Content Determination

This procedure used a microwave oven (National Model NN7806, Japan) to evaporate the moisture content present in the casein curd. About 5 g of dewatered curd was sandwiched between two sheets of filter paper. The curd sample was then placed in a porcelain bowl and dried in the microwave oven for 15 minutes on a high power setting. After drying the sample was cooled in a dessicator for 30 minutes and then weighed to the nearest 0.01 g on a Mettler PE1600 balance. The moisture content of the samples were calculated on a dry basis (kg water/kg dry solids). Five replicates were taken for each batch of curd and the mean moisture content was used in all calculations.

3.3.2.2. Drying Rate Determination of Casein Curd

Six batches of mineral acid casein curd were made at standard conditions (Section 3.1.1). The initial moisture content of the curd samples were determined using the procedure in Section 3.3.2.1. Using this information the initial moisture contents of the samples was standardized by squeezing out water from the wetter samples.

The tunnel drier (described in Section 3.2.1) was stabilized for one hour at the required drying conditions. The drier was operated at an inlet dry bulb temperature (DBT) of 80±1°C, an air velocity of 5.0±0.1 m/s and at ambient humidity.

About 360 g of curd sample was spread evenly on the drying tray. The tray was then connected to the weighing system and suspended in the drying chamber. Drying was begun and the moisture loss of the sample was recorded on the computer until the mass loss was less than 0.01 g per 3 minutes.

The dried sample was divided into ten portions which were dried in an air oven (as in Section 3.3.1.2) at 105°C for at least 15 hours to determine the moisture content. A Mettler AE160 balance was used in all weighings.

Appendix 3.1 shows the sample calculations in determining the moisture content of the sample at any given time during drying. A plot of moisture content versus time (drying curve) was obtained for each drying run. The drying rate curve was obtained by taking the slope of the drying curve at each data point (drying rate) and plotting against the corresponding moisture content.

3.3.3. Fluidized Bed Drying of Casein Curd

Pilot plant (Section 3.1.2) and commercial (Section 3.1.3) casein curds made at standard manufacturing conditions were used in these experiments. About 5 kg of sample was placed in a plastic bag. The vibrator was turned on at half setting (about 5 strokes per second) and the bag of curd was emptied into the drier. The filter bag was replaced and the air flow was turned on. The correct number of heaters to reach the desired air inlet temperature was turned on. The first curd sample was taken after the drier reached the standard inlet temperature of 81^{O}C at an air velocity of 1.6 m/s. This usually took about 8 minutes. The inlet air was at ambient humidity which was determined using a sling psychrometer. The humidity of the room varied from 0.0060 to 0.0118 kg water/kg dry air. Curd was sampled periodically throughout the drying period. Each sample was sealed in poly-nylon bag until moisture content determination was carried out. The drying time was about 45 minutes to reduce the curd moisture content to below 0.100 kg water/kg dry solids. The moisture contents of the samples were determined as in Section 3.3.2.2.

3.3.4. Measurements in a Commercial Casein Dry Processing System

Measurements at Various Stages of an NDA Vibrated Bed Drier. Casein temperatures and moisture contents were measured at various stages through an NDA vibrated bed drier (Tui Milk Products Ltd., Longburn). The NDA vibrated bed drier consisted of a predrier (2 decks) and a final drier (4 decks). The lengths of the decks of the predrier and final drier were 6.5 meters. Measurements were taken at the following locations: a) the top deck of predrier about 0.2 m from the point of entry of dewatered curd; b) near the end of the top deck (5.44 m from entry point); c) on the second deck of the predrier 1.25 m from the entry of casein from the top deck; d) at the end of the second deck of the predrier; e) on the top deck of the final drier 4.38 m from entry of casein from the predrier; f) at the end of the second deck of the final drier; and g) out of the fourth deck of the final drier The temperatures were determined by placing a 100 ml sample in a plastic container embedded into a thick polystyrene block to prevent heat loss during measurement. A temperature probe was inserted into the sample and a reading was made after the probe had equilibrated. The moisture content of the samples were determined using the procedure in Section

3.3.2.2.

Moisture Content as a Function of Particle Size from the Dry Processing System. Moisture content as a function of particle size was determined for casein leaving the NDA predrier and final drier, Niro fluidized bed drier, cooler and tempering bin. About 40 g of sample was sieved immediately for 10 minutes using a mechanical shaker. The different size fractions were immediately sealed in plastic bags and stored until moisture content could be determined. The moisture content of the samples were determined as in Section 3.3.2.2.

Moisture Content as a Function of Particle Size with Different Storage Time After Drying. Moisture content as a function of particle size was also measured for casein immediately leaving the NDA final drier and at different storage times after drying. The sieving and moisture content determination were as described above.

3.3.5. Physical Changes on Drying a Single Casein Particle

Seed Volume Displacement. A procedure was developed to measure the actual volume of casein particles regardless of the shape. This uses the same technique as the rapeseed displacement method used for bread loaf volume determination (AACC, 1962).

Maku lotus seeds were used for the displacement procedure because the very small, spherical and uniform size (0.8-1.0 mm) of the seeds as compared to rapeseed would be expected to give better results.

The seed volume displacement procedure was first used in measuring the volume of different sized spherical objects for comparison. The experimental set-up is shown in Figure 3.5. The container used was a specially fabricated polycarbonate cylinder. The inside dimensions were diameter of 2.504 cm and height of 5.012 cm giving a volume of 24.68 cm^3. Seeds were first put in the empty container through the funnel. The mass of the seeds in the container was then determined. The object to be determined was put into the container with some seeds on the bottom and the rest of seeds were replaced. The mass of the seeds displaced was then determined. Using equations below the volume of the object can be obtained,

$$V_2 = V_1 \times (W_2/W_1) \tag{3.1}$$

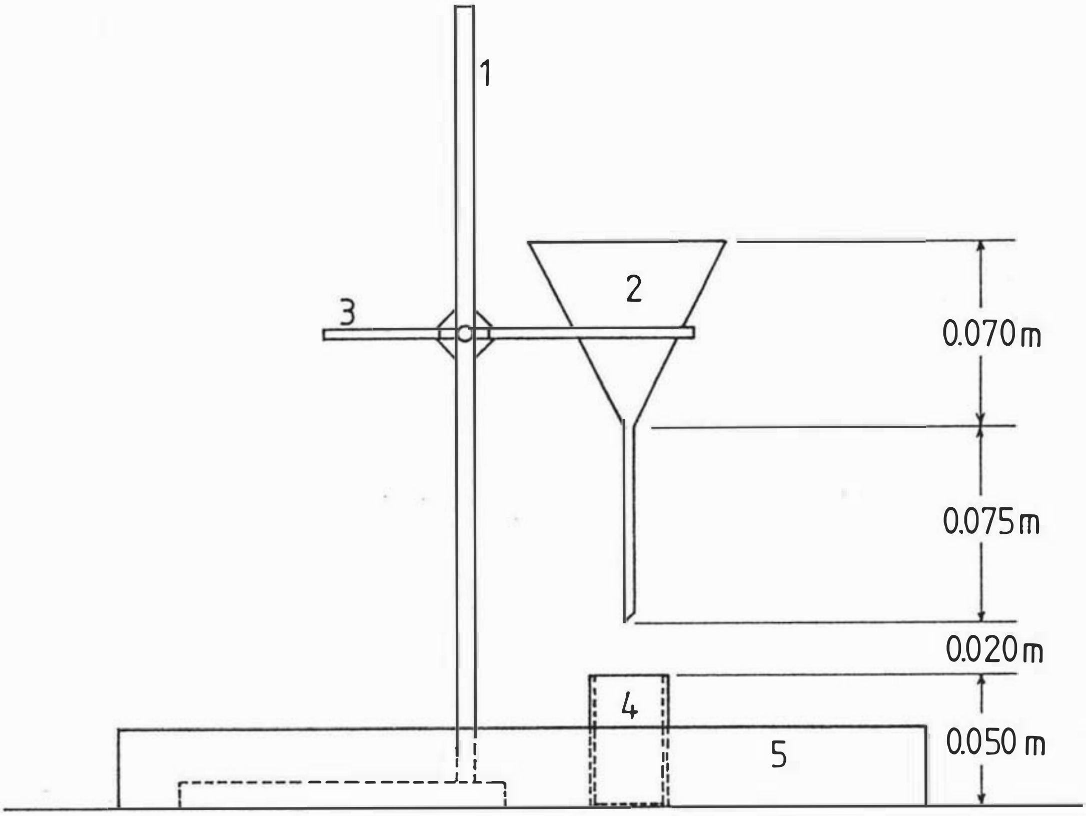


Figure 3.5. Experimental set-up for the seed volume displacement determination showing iron stand (1), glass funnel (2), iron clamp (3), polycarbonate cylinder (4) and stainless steel container (5).

where: V_1 = volume of the container (cm^3)
W_1 = total mass of seeds from the container (g)
W_2 = mass of displaced seeds (g)
V_2 = volume of the particle (cm^3)

The results showed that the displaced volume of particles was always higher than the actual volume. The actual volume was the volume calculated using the mean diameter of the spherical object. A regression equation was derived for predicting the actual volume from the seed volume displaced,

$$V_a = -0.043 + 0.949 V_d \tag{3.2}$$

where: V_a = actual volume of object (cm^3)
V_d = seed volume displaced (cm^3)

This equation was applicable for particles with a volume between 0.45 cm^3 and 3.88 cm^3.

Percentage Volume Measurements for Wet and Dry Casein Particles. Big lumps (1-2 cm in mean diameter) of different types of casein curd were selected for this study. The initial volumes of the particles were determined using the seed volume displacement procedure. The casein curd particles were then dried in a tunnel drier (described in section 3.2.1) at an inlet dry bulb temperature of 90°C, an air velocity of 5.0 m/s and at ambient humidity. A high drying temperature was used to speed up the drying process. After 4-6 hours of drying, the casein particles were removed and the particle volume determined as before. The initial and final masses of the particles were recorded. The moisture content of the dried particles were determined using the procedure from Section 3.3.2.2.

From the initial and final volumes of the particle, the percent shrinkage was calculated. The percentage volume of the casein, water and air components of the particle were also determined. The volumes of the casein and water components were obtained from the initial and final masses, the initial and final moisture contents of the particle and the densities of the components (Munro, 1980; Ranznevic, 1978). The volume of the air component was determined by taking the difference between the particle volume and the volumes of the casein and water components. Appendix 3.2 shows sample calculations for this procedure.

Percentage Volume Measurements of a Drying Casein Particle. Pilot plant lactic casein curd was also dried in the tunnel drier using the same conditions as above. The initial mass was recorded and the initial volume of the casein particle was determined using the seed volume displacement procedure. At various times during the drying process, the casein particle was rapidly removed from the drier and the mass and volume determined before returning to the drier. The total elapsed time from removal of the particle to returning to the drier, was not more than 2 minutes. The elapsed time during the volume determination was not added to the total drying time. After 5 hours of drying, the casein particle was removed and the mass, volume and moisture content were determined. Percentage volume of the particle and the different components were also calculated as before.

3.3.6. NMR Measurements of Casein Particles

PGSE NMR Experiments on Casein Particles. Different types of casein from NZDRI were dried in a fluidized bed drier (described in Section 3.2.2) using the standard conditions described in Section 3.3.3. During the drying process samples were withdrawn from the drier at various times and sealed in poly-nylon bags immediately. Representative samples from each bag were taken for moisture content determination as in Section 3.3.2.2. The samples were stored in a cool store until use. The duration between storage of samples and NMR measurements did not exceed one week.

Particles of 0.5-1.0 mm were selected from the bags and placed loosely packed inside a 3 mm test tube. The end of the tubes were sealed using teflon tape. The measurements were done one at a time until all the samples were measured.

Determination of the transverse relaxation time (T_2) and self diffusion coefficient (D) of all the samples were carried out using a $90^o/180^o$ pulse sequence. The signals from the NMR measurements can be partially resolved using a Fourier Transform PGSE in a 'relatively' homogeneous field. However, full resolution of the various proton-bearing molecular species was not possible. All measurements were carried out on the NMR apparatus (described in Section 3.2.3) by Dr. Phil Back from the Department of Physics and Biophysics at Massey University.

In a separate experiment samples of pilot plant mineral acid casein curd were obtained from NZDRI and dried in the fluidized bed drier as before. When the curd was partly dried a sample was taken from the drier. The sample was rushed to the NMR room for immediate measurement of its self diffusion coefficient. The self diffusion coefficient of the sample was measured at various times after drying. The moisture content of a representative sample from the same batch was also determined.

NMR Imaging Experiments on a Casein Particle. The proton and diffusion maps of a wet casein particle was determined using a $90^{o}/180^{o}$ pulse sequence on the same NMR apparatus but with a separate imaging probe. Measurements for the redistribution of moisture in a partly dried casein were carried out because of the very fast moisture equilibration within the particle.

3.3.7. Casein Thermal Sensitivity Experiments

The effects of moisture content, temperature and time on some properties of casein were studied. A 2^3 factorial experiment was devised to determine which of these factors including interactions affected the thermal sensitivity of casein. Colour and solubility of casein were used as indices for thermal sensitivity. The factorial experiment used high and low levels of each factor (Table 3.1).

The time of 1/3 hour (20 minutes) was the minimum time taken for the centre of the sample to reach the required temperature. Earlier trials at $140^{o}C$ and $120^{o}C$ indicated very severe denaturation of the wet samples and so $100^{o}C$ was chosen as the upper limit.

Dewatered mineral acid casein curd was obtained from NZDRI. Samples of dewatered curd were retained for the experiment. The rest of the casein curd was dried in the fluidized bed drier at an air inlet temperature of $70^{o}C$, an air velocity of 1.6 m/s and at ambient humidity. After the required drying time, the dried casein was taken out and used for the experiment. The moisture content of representative samples of the wet and dried casein were determined as in Section 3.3.2.2.

Wet and dried samples were packed in poly-nylon bags for the $60^{o}C$ temperature (water bath) and tin cans for the $100^{o}C$ temperature (oil bath). The samples were immersed in the specific baths for the required time, after which the samples were taken out and cooled in running water.

Additional experiments were also added at selected middle level values of moisture content, temperature and time (Table 3.2) making a total of 19 samples. The samples in the tin cans were taken out and stored in poly-nylon bags. All the samples were dried to approximately 10% moisture (w.b.) in a vacuum oven (described in Section 3.3.1.2) at 60-$65^{o}C$ and 750 mm Hg of vacuum. After drying, the samples were milled in a grinder (Zip Industries, New Zealand) to 500 μm for the solubility test and to 250 μm for the colour measurements. The solubility test was carried out using the procedure in Appendix 3.3. The colour measurements were carried out in a HunterLab Colorquest (Hunter Associates Laboratory Inc., USA) attached to an IBM compatible personal computer (MCS Computer, Taiwan). Figure 3.6 shows the block diagram for the procedure used in these experiments.

Table 3.1. 2^3 factorial design for the thermal sensitivity experiment at different moisture content, temperature and time.

Factor	Low level	High Level
Moisture Content (% w.b.)	14	56
Temperature (°C)	60.0±0.5	100±1
Time (hour)	1/3	2

Table 3.2. Additional experiments on thermal sensitivity of casein at selected values of moisture content, temperature and time.

Experiment Number	Moisture Content (% w.b.)	Temperature (°C)	Time (hr)
9	14	80	2
10	56	80	2
11	30	60	2
12	30	100	1/3
13	30	100	2
14	30	80	2
15	56	100	1
16	43	100	1
17	30	100	1
18	19	100	1
19	14	100	1

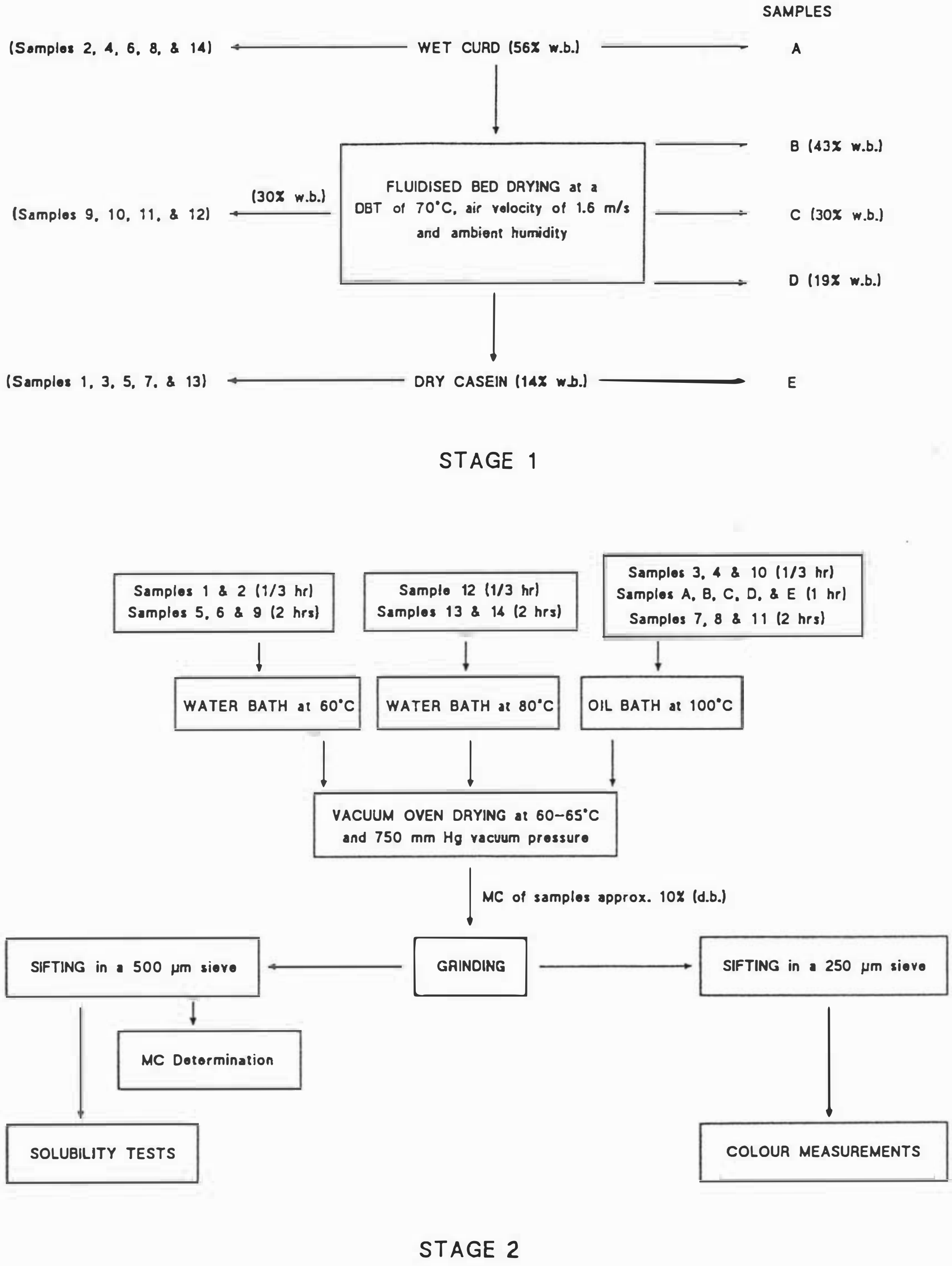


Figure 3.6. Block diagram of the procedure (Stages 1 and 2) used for the thermal sensitivity experiments on casein.

CHAPTER 4
CASEIN DESORPTION ISOTHERMS

4.1. CASEIN DESORPTION ISOTHERMS AT DIFFERENT TEMPERATURES

4.1.1. Desorption Isotherms

Three types of casein were made in the laboratory (Section 3.1.1) and their desorption isotherms were determined at different temperatures (Section 3.3.1). The desorption isotherms of the three types of casein at different temperatures were sigmoid in shape and of type II according to the BET classification (Figures 4.1, 4.2 and 4.3). An increase in temperature caused a decrease in EMC at the same water activity as expected from thermodynamics (Kinsella and Fox, 1986), and as reported by other researchers for milk proteins (Heldman *et al.*, 1965; Berlin *et al.*, 1970; Hermansson, 1977).

At a given water activity and temperature the EMCs for the three types of casein decreased in the order mineral acid > rennet > lactic. At each temperature the difference between mineral acid and lactic caseins is about 0.02-0.03 kg water/kg dry solids, at each water activity. These differences in water sorption can be attributed to differences in molecular composition and molecular packing (or porosity) of the three types of casein. Rennet casein differs in composition from the two acid caseins in that it has a higher mineral content, typically 7.8% ash as compared to 1.8% ash for the acid caseins, and it also lacks the hydrophilic glycomacropeptide removed by rennet cleavage. Ruegg *et al.* (1974) compared the moisture desorption isotherms of micellar casein and rennet casein, which would have similar mineral contents, and concluded that the loss of the hydrophilic glycomacropeptide in rennet casein led to lower moisture sorption. Lactic and mineral acid caseins have similar compositions except that lactic casein contains microbial starter cells. The differences in moisture sorption between these two caseins is therefore attributed to differences in molecular packing, i.e. in access of water to binding sites on the casein. Espie *et al.* (1984) ranked the caseins in order of decreasing ease of drying as lactic with a gas producing starter > lactic with a non-gas producing starter > mineral acid > rennet. Ease of drying is a rate measurement whereas moisture sorption is an equilibrium measurement so it is not necessarily surprising that the rank orders are different for the two properties.

Figure 4.3 also allows comparison of the desorption isotherms for rennet casein of Ruegg *et al.* (1974) at 25^{o}C, Hardy & Steinberg (1984) at 20^{o}C and our experiments at

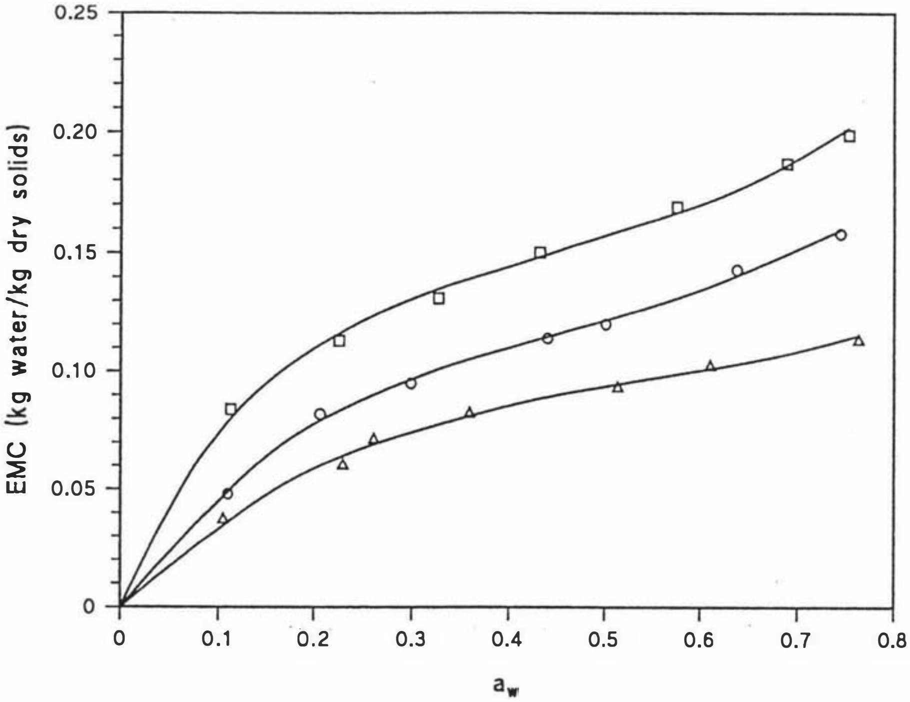


Figure 4.1. Desorption isotherms of mineral acid casein at 27°C (□), 53°C (○) and 80°C (△). Data points are a mean of three observations.

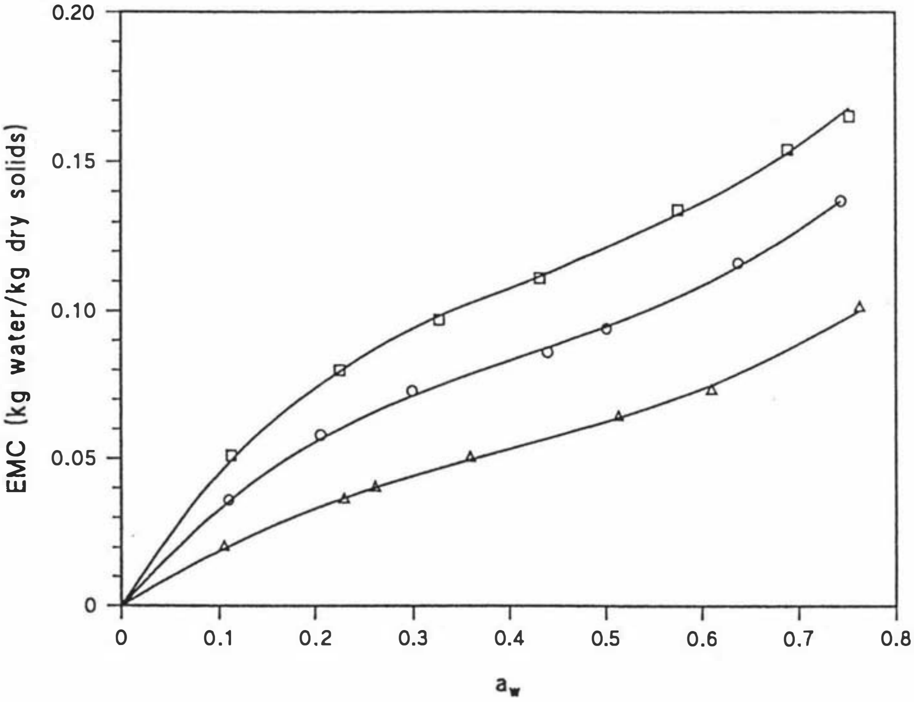


Figure 4.2. Desorption isotherms of lactic casein at 28°C (□), 55°C (○) and 80°C (△). Data points are a mean of three observations.

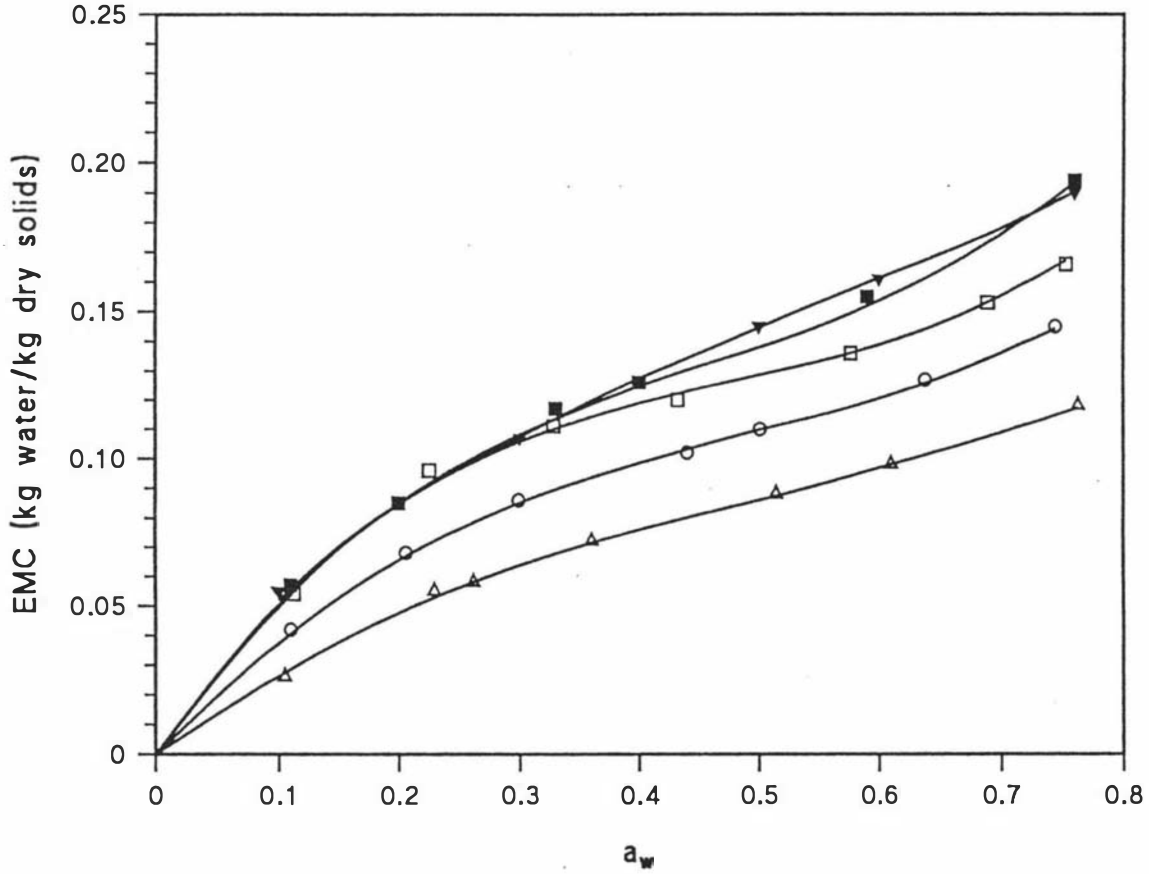


Figure 4.3. Desorption isotherms of rennet casein at 28°C (□), 55°C (○) and 80°C (△). Data points are a mean of three observations. Desorption isotherms from other reports at 20°C (■) (Hardy & Steinberg, 1984) and 25°C (▼) (Ruegg et al., 1974) are also shown.

28^oC. Each study used somewhat different casein preparation and isotherm determination methods and Ruegg *et al.* (1974) and Hardy & Steinberg (1984) both lyophilized their casein samples and rewetted them before measuring the casein desorption isotherms. Agreement between the three studies is reasonable considering the different methods used in sample preparation and the different temperatures of the isotherms.

Figure 4.4 shows various adsorption and desorption isotherms of mineral acid casein at 27^oC. The casein used in the adsorption isotherm was freeze dried at a plate temperature of 60^oC rather than hot air dried to reduce the possibility of conformational changes and rearrangements of the protein structure. The two desorption isotherms for different casein preparations are similar though in the a_w range 0.3-0.7 their EMCs differ by as much as 0.01 kg water/kg dry solids. The adsorption isotherm has a similar shape to the desorption isotherms but is on average about 0.02 kg water/kg DS lower. Hysteresis loops with adsorption isotherms lower than desorption isotherms have often been reported for milk proteins and the difference between the two curves is typically 0.01-0.03 kg water/kg DS (Rao & Das, 1968; Berlin *et al.*, 1969; Ruegg *et al.*, 1974; Hardy & Steinberg, 1984). Adsorption-desorption hysteresis is thought to reflect structural rearrangements which occur even on freeze drying and which reduce the accessibility of polar groups and micropores in the protein matrix to water molecules (Kinsella & Fox, 1986).

4.1.2. Equation Fitting of Isotherms

Labuza (1968) discussed the selection and usefulness of isotherm equations. Two major selection criteria for engineering calculations are accuracy and simplicity. For the prediction of drying times, or the shelf life of packaged foods, the user is interested in an equation which fits closely to the experimental data rather than in the correctness of the theory on which the equation is based. An equation with the smallest number of constants is usually the simplest to use.

With these criteria in mind, six equations from Boquet *et al.* (1978) which could be transformed into a regression form were used in fitting the isotherms of the three types of casein. The six equations were linearized and grouped in the following forms:

$$M_e = I + S\, f(a_w) \qquad \text{Bradley and Kuhn equations}$$

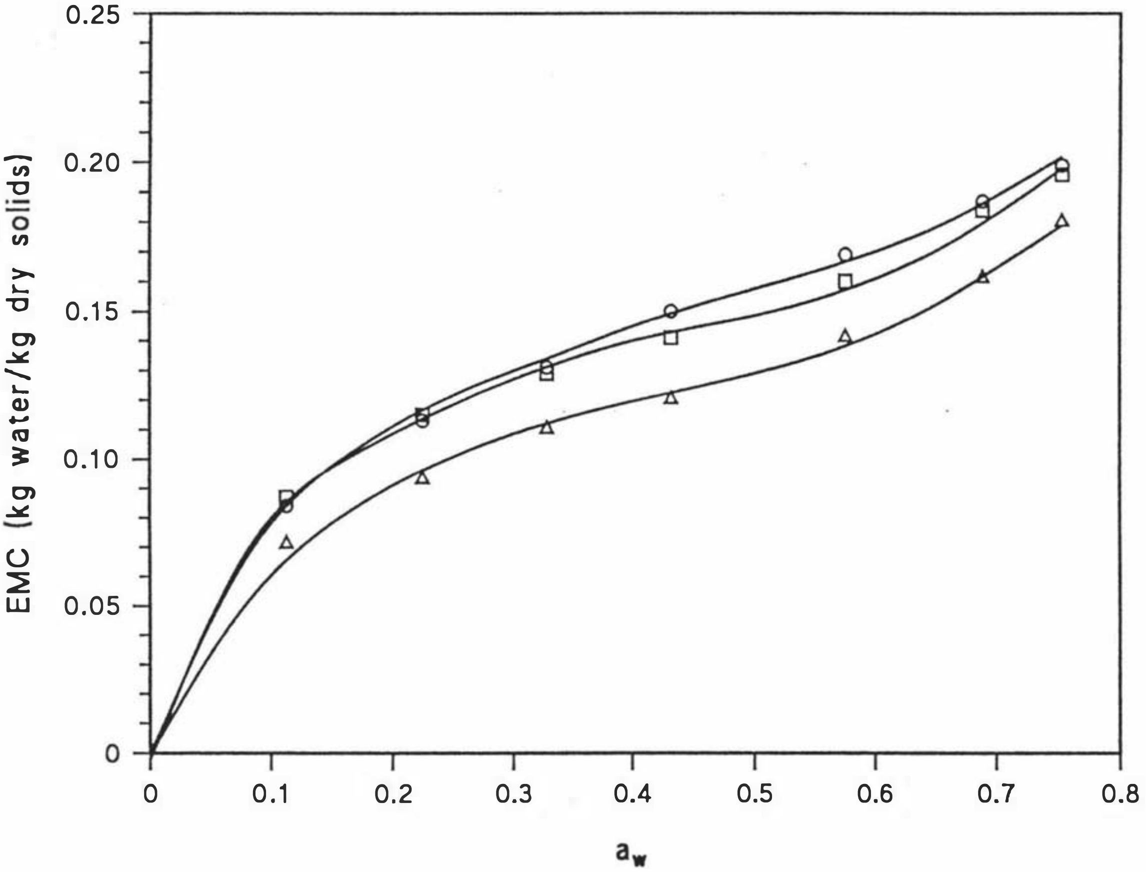


Figure 4.4. Various sorption isotherms of mineral acid casein: desorption isotherms from two different preparations at 27°C (○, □); and adsorption isotherm of freeze dried casein at 27°C (△).

$$\ln M_e = I + S\, f(a_w)$$ Caurie, Halsey, Henderson and Oswin equations

where M_e is the EMC, I and S denote the intercept and slope of the regression line and f stands for a functional relationship.

Consistently high coefficients of determination (r^2) of the regression under all experimental conditions were used as the basis for selecting the best equation. Table 4.1 presents the r^2 values of the six equations for the three types of casein at various temperatures. The Bradley and Henderson equations gave consistently higher r^2's than the other equations. However when the MRPD values were calculated for the two equations, the Henderson equation gave much lower MRPDs for most of the isotherms. In addition, at zero a_w the Bradley equation predicted negative EMCs (range -0.007 to -0.042 kg water/kg DS for the nine isotherms) whereas the Henderson equation predicted low positive EMCs (range 0.0001 to 0.029 kg water/kg DS for the nine isotherms). The Henderson equation was therefore chosen as most appropriate for fitting the isotherms.

Boquet *et al.* (1978) found that the Oswin equation best described the isotherms of a range of food proteins followed by the Henderson and Bradley equations in that order. The proteins included in their study were egg albumin, fish protein concentrate, gelatin, lactoglobulin and serum albumin (horse). A number of researchers have reported that the Henderson equation could adequately describe moisture sorption isotherms (Rockland, 1957; Fito & Sanz, 1974; Igbeka & Blaisdell, 1982).

4.1.3. Temperature Dependence of Isotherms

Equations for predicting the effect of temperature on sorption isotherms of foods are important because of the limited data available at higher temperatures. Such equations make it possible to interpolate and extrapolate (with caution) the limited available sorption isotherm data to other temperatures, and are particularly useful for desorption operations such as drying which occur at higher temperatures.

Table 4.2 shows the slopes and intercepts for regression of the Henderson equation to desorption isotherms for all caseins and temperatures. Generally the slopes increase with temperature and the intercepts decrease with temperature for each casein type. The constants in Table 4.2 for each casein type were related to temperature by linear, logarithmic and exponential regressions. The regression with the highest r^2 was chosen

Table 4.1. Coefficients of determination (r^2) for the six equations from Boquet *et. al.* (1978) fitted to the desorption isotherms.

Temperature (^{o}C)	EQUATIONS Bradley	Caurie	Halsey	Henderson	Kuhn	Oswin
Mineral Acid Casein						
27	0.986	0.950	0.942	0.996	0.864	0.982
53	0.972	0.887	0.884	0.967	0.833	0.942
80	0.921	0.830	0.820	0.942	0.716	0.901
Lactic Casein						
28	0.992	0.938	0.932	0.993	0.886	0.976
55	0.994	0.938	0.937	0.989	0.910	0.978
80	0.993	0.944	0.944	0.994	0.935	0.985
Rennet Casein						
28	0.950	0.850	0.848	0.945	0.814	0.914
55	0.980	0.900	0.896	0.978	0.844	0.954
80	0.975	0.853	0.848	0.959	0.819	0.924

Table 4.2. Slopes (S) and intercepts (I) for regression of the Henderson equation[a] to the desorption isotherms.

Temperature (^{o}C)	Slope	Intercept
Mineral Acid Casein		
27	0.347	2.884
53	0.456	2.664
80	0.429	2.361
Lactic Casein		
28	0.468	2.669
55	0.517	2.459
80	0.605	2.072
Rennet Casein		
28	0.416	2.702
55	0.483	2.565
80	0.564	2.103

[a] $\ln M_e = I + S \ln(-\ln(1-a_w))$

as the functional relationship for temperature for that casein type. The average value of each constant over the temperature range was also evaluated to see whether it could describe the isotherm adequately and so reduce the number of constants in the mathematical model.

The modified Henderson equations which describe the isotherms of different types of casein as a function of temperature are shown in Table 4.3. The three-constant equations use a mean value for slope whereas the four-constant equations relate the slopes to temperature by either logarithmic or exponential regressions. The intercepts were related to temperature by linear regression for all equations. The MRPDs of the Henderson equations in Tables 4.2 and 4.3 from the experimental desorption isotherms were calculated (Table 4.4). As expected the three-constant modified Henderson equations gave higher MRPDs than the four-constant equations. The three-constant equations are simpler but less accurate. However, the highest MRPD for any of the three-constant equations was only 10.6% which is still a satisfactory result as shown below (Figure 4.5). The unmodified Henderson equations give the lowest MRPDs, as expected, but these use a separate equation at each temperature and so do not incorporate temperature dependence.

Figure 4.5 plots experimental isotherm data and compares them with the curves predicted by the three-constant Henderson equations for the conditions which gave the lowest and highest MRPD. Even the worst fitting curve (highest MRPD) gave reasonable agreement between experimental and predicted EMCs with a maximum deviation of less than 0.01 kg water/kg DS over the whole water activity range. It is concluded that the three-constant modified Henderson equations can satisfactorily describe the desorption isotherms of the three types of casein as a function of temperature. Similar conclusions were reached by Iglesias & Chirife (1976a) and Diamante & Munro (1990) who developed three-constant equations to describe the isotherms of several food products adequately as a function of temperature.

4.2. MONOLAYER MOISTURE CONTENTS OF CASEINS

The monolayer moisture contents of the caseins were obtained using the two-constant BET equation (Brunauer *et al.*, 1938),

$$\frac{a_w}{M_e(1-a_w)} = \frac{1}{M_m C} + \frac{(C-1)a_w}{M_m C} \qquad (4.1)$$

Table 4.3. Best fit three-constant and four-constant modified Henderson equations[a] for the desorption isotherms as a function of temperature[b].

Casein	Modified Henderson Equation
Mineral acid	
	Three-constant
	$\ln M_e = 3.163-0.00988T + 0.411\ln(-\ln(1-a_w))$
	Four-constant
	$\ln M_e = 3.163-0.00988T + 0.1766\, T^{0.216} \ln(-\ln(1-a_w))$
Lactic	
	Three-constant
	$\ln M_e = 3.021-0.0114T + 0.530\ln(-\ln(1-a_w))$
	Four-constant
	$\ln M_e = 3.021-0.0114T + 10^{(-0.395+0.00214T)}\ln(-\ln(1-a_w))$
Rennet	
	Three-constant
	$\ln M_e = 2.907-0.00672T + 0.483\ln(-\ln(1-a_w))$
	Four-constant
	$\ln M_e = 2.907-0.00672T + 10^{(-0.453+0.00253T)}\ln(-\ln(1-a_w))$

[a] Three constant equations use a mean slope; four constant equations express slope as a function of temperature

[b] T = temperature of the isotherm (^{o}C)

Table 4.4. Mean relative percentual deviation (MRPD) of various best fit Henderson equations from the experimental desorption isotherms.

Temperature (°C)	Henderson Equation[a]	Modified Henderson Equation Three-constant[b]	Modified Henderson Equation Four-constant[b]
Mineral Acid Casein			
27	1.52 %	5.21 %	1.89 %
53	5.02 %	5.05 %	5.08 %
80	7.02 %	7.42 %	7.27 %
Lactic Casein			
28	2.60 %	5.27 %	3.96 %
55	3.56 %	7.26 %	7.18 %
80	3.21 %	10.65 %	4.62 %
Rennet Casein			
28	6.80 %	7.88 %	7.18 %
55	4.84 %	5.01 %	4.97 %
80	8.21 %	9.39 %	8.35 %

a Henderson equations given in Table 4.2, i.e. Temperature dependence not incorporated.

b Henderson equations given in Table 4.3.

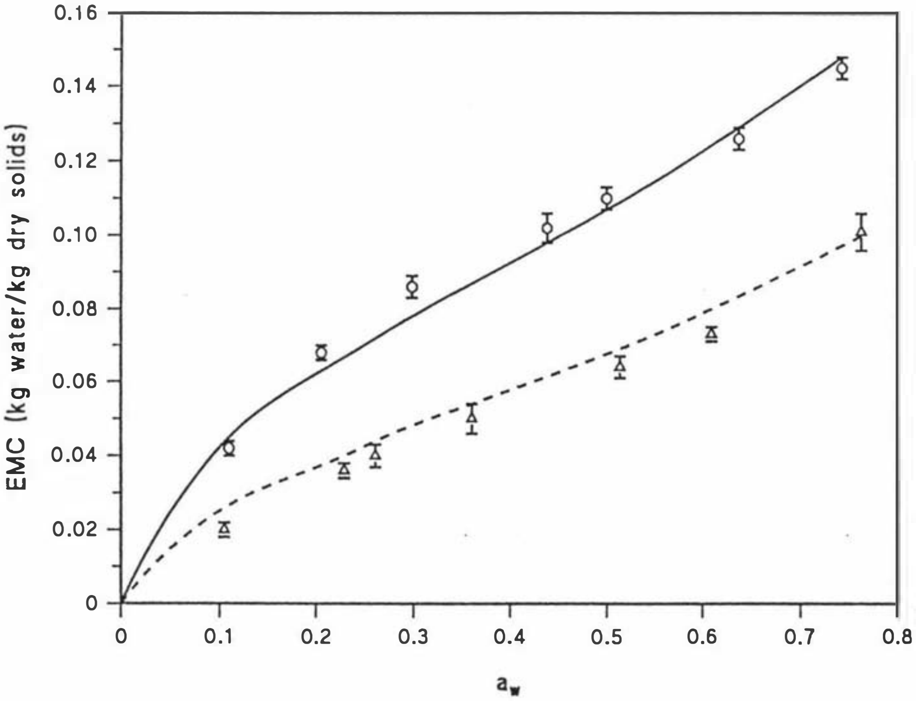


Figure 4.5. Best fitting (o, ————) (lowest MRPD; rennet casein, 55°C) and worst fitting (Δ, – – – –) (highest MRPD; lactic casein, 80°C) desorption isotherm curves from the three-constant modified Henderson equations. Experimental data (o, Δ) are shown as a mean with 95% confidence limits.

where: M_m = monolayer moisture content (kg water/100 kg DS)
C = energy constant for heat of sorption of the monolayer

Linear regression of $a_w/[M_e(1-a_w)]$ against a_w for all isotherms up to $a_w = 0.44$ gave high r^2 values (Appendix 4.1). The slopes and intercepts of these regression lines enable calculation of M_m and C. Appendix 4.2 shows sample calculations for obtaining the BET parameters. Table 4.5 summarizes the parameters from the BET regression for the three types of casein at different temperatures. Kuntz & Kauzmann (1974) quoted a BET monolayer moisture content of 0.0550 kg water/kg DS for casein and a range of 0.0565 to 0.0952 kg water/kg DS for other proteins using adsorption isotherm data at 25°C. Ruegg *et al.* (1979) reported BET monolayer moisture contents from 0.0484 to 0.0618 kg water/kg DS for micellar casein from a range of fresh and heat treated milks (adsorption data at 25°C). The values obtained in this study from desorption isotherms at 27-28°C were 0.089, 0.070 and 0.077 kg water/kg DS for mineral acid, lactic and rennet caseins, respectively. Since desorption moisture content values are typically 0.02 kg water/kg DS higher (range 0.01-0.03 kg water/kg DS higher) than adsorption values the results from these studies are in reasonable agreement.

The results indicate that M_m decreases with increasing temperature. Heldman *et al.* (1965) reported a similar trend for M_m values from the desorption isotherms of a range of heat treated spray dried milks at different temperatures.

4.3. HEATS OF DESORPTION OF CASEINS

Sorption isotherms determined at different temperatures can be used to estimate the strength of binding, provided the substrate is not altered by temperature. The most common method for determining the energy of water binding is based on the Clausius-Clapeyron equation using sorption data from at least three different temperatures. The integral form of the equation is,

$$\ln a_w = \frac{-\Delta H_s}{RT} + \text{Constant} \qquad (4.2)$$

where:

$\Delta H_s = H_s - H_w$ = isosteric heat of sorption (kJ/mole)
H_s = heat of sorption (kJ/mole)
H_w = heat of condensation of pure water (kJ/mole)

Table 4.5. Parameters from the BET regression for the three types of casein at different temperatures.

Temperature (^{o}C)	I	S	r^2	M_m (kg water/kg DS)	C
Mineral Acid Casein					
27	0.169	11.12	0.994	0.089	67.0
53	0.732	13.48	0.965	0.070	19.4
80	1.666	13.91	0.959	0.064	9.3
Lactic Casein					
28	0.785	13.56	0.985	0.070	18.3
55	1.108	17.48	0.968	0.054	16.8
80	3.428	21.40	0.988	0.040	7.2
Rennet Casein					
28	0.613	12.44	0.949	0.077	21.3
55	1.026	14.54	0.968	0.064	15.2
80	2.905	12.82	0.929	0.064	5.4

R = universal gas constant (8.31 J/mole^{o}K)
T = absolute temperature (^{o}K)

Plots of ln a_w versus 1/T can be used to determine ΔH_s and so H_s at a range of moisture contents. For each type of casein H_s decreases with increasing moisture content and approaches the heat of evaporation (or condensation) of pure water (43.1 kJ/mole) at a moisture content of 0.30 kg water/kg DS (Figure 4.6). Similar results were obtained by Kuntz & Kauzmann (1974) for different proteins, by Iglesias & Chirife (1976b) for cooked and raw chicken muscle and by Igbeka & Blaisdell (1982) for bologna. The results indicate that mineral acid casein had the highest heat of desorption at a given moisture content. This suggests that the remaining moisture in mineral acid casein would be most difficult to evaporate during the final stage of drying.

4.4. EFFECT OF CASEIN MANUFACTURING CONDITIONS ON EMC

Mineral acid casein was prepared in the NZDRI pilot plant under 24 different sets of manufacturing conditions (Table 4.6). The adsorption EMC of each dried casein sample was then determined at a_w = 0.432 and 30^{o}C (Section 3.3.1). Most of the experimental variables had no significant effect on EMC. However, drying conditions had a major effect on EMC as shown in Table 4.7, which also includes EMCs from the adsorption isotherm of freeze dried casein and the desorption isotherm of casein which had never been dried. The major trend from Table 4.7 is clearly that the more severe the drying conditions the lower the EMC. Casein which had never been dried (desorption isotherm) has the highest EMC. Freeze dried casein has a 0.02-0.03 kg water/kg DS lower EMC. Freeze drying leaves a very porous casein structure which facilitates moisture adsorption. Casein which had been hot air dried in two stages, initially in a ring drier with final drying at a low inlet air temperature in a fluidized bed drier, had an EMC about 0.03 kg water/kg DS lower than freeze drying. Casein which had been dried totally in the ring drier had the lowest EMC, with a trend for lower EMC at higher air inlet temperature. Hot air drying produces a much lower casein volume than freeze drying. The lower volume particles also appear less porous.

Heldman *et al.* (1965) discussed the mechanisms of moisture sorption by dried milk including the protein components. Moisture sorption by proteins is not merely a surface phenomenon. Water molecules penetrate into the protein to be adsorbed by hydrogen bonding at polar sites, e.g. around polar side chains, and also to form multilayers in the protein held by van der Waals forces. Moisture sorption to proteins therefore depends on the number of polar sites, on access of water molecules to these

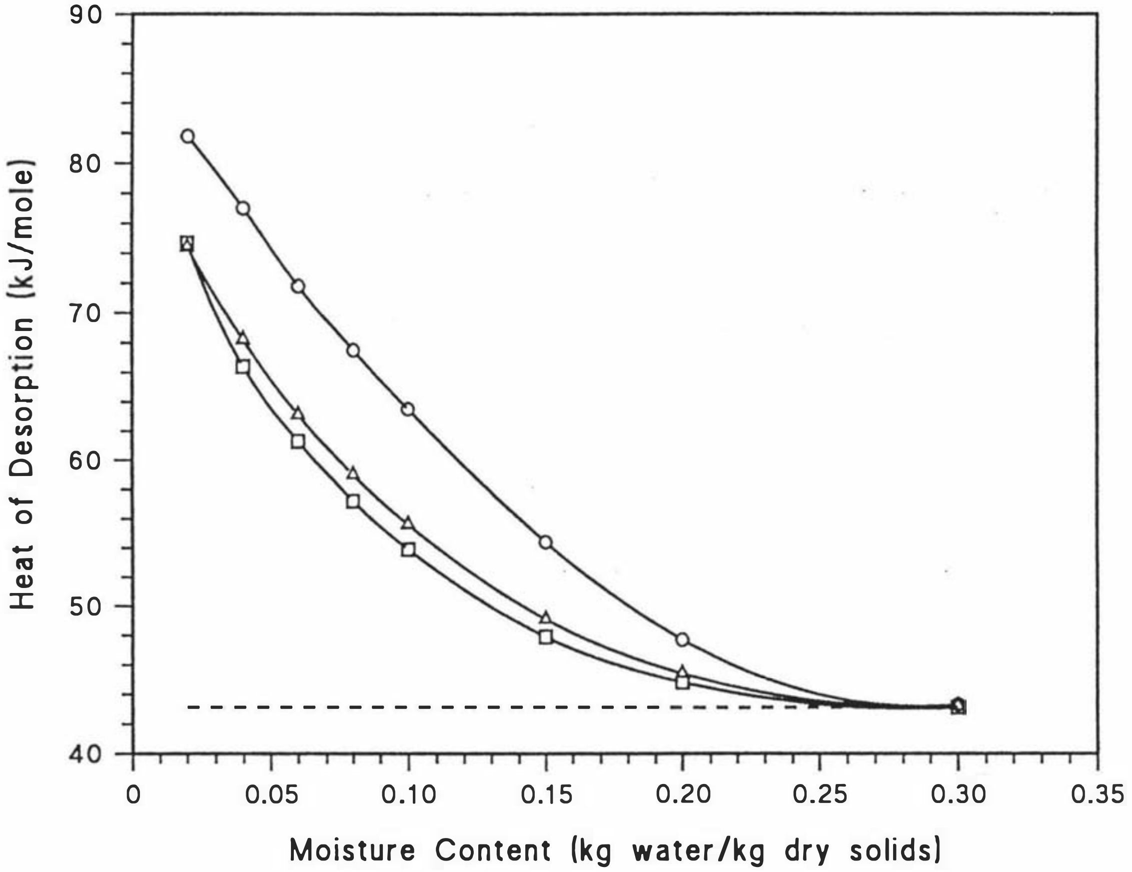


Figure 4.6. Heat of desorption as a function of moisture content for mineral acid casein (○), lactic casein (Δ) and rennet casein (□). The heat of evaporation of pure water is 43.1 kJ/mole (– – – – –).

Table 4.6. Effect of manufacturing conditions on adsorption EMC for mineral acid casein prepared on pilot scale equipment.

Pasteurisation (°C)	Precipitation pH	Cook temp. (°C)	Wash water ratio[a]	Hot wash temp. (°C)	Drier used[b]	Drier air inlet temp (°C)	EMC[c] (kg water/ kg DS)
72	4.65	45	0.3	60	Ring/Glatt	150/50	0.0911
78	4.65	45	0.3	80	Ring	150	0.0853
72	4.65	55	0.3	80	Ring/Glatt	220/70	0.0888
78	4.65	55	0.3	60	Ring	220	0.0763
72	4.65	45	0.3	60	Ring	220	0.0843
78	4.65	45	0.3	80	Ring/Glatt	220/70	0.0884
72	4.65	55	0.3	80	Ring	150	0.0875
78	4.65	55	0.3	60	Ring/Glatt	150/50	0.0894
72	4.65	45	0.5	80	Ring	220	0.0840
78	4.65	45	0.5	60	Ring/Glatt	220/70	0.0876
72	4.65	55	0.5	60	Ring	150	0.0844
78	4.65	55	0.5	80	Ring/Glatt	150/50	0.0884
72	4.65	45	0.5	80	Ring/Glatt	150/50	0.0894
78	4.65	45	0.5	60	Ring	150	0.0849
72	4.65	55	0.5	60	Ring/Glatt	220/70	0.0865
78	4.65	55	0.5	80	Ring	220	0.0804
72	4.50	50	0.5	60	Ring	180	0.0773
78	4.50	50	0.5	60	Ring	180	0.0781
72	4.75	50	0.5	60	Ring	180	0.0845
78	4.75	50	0.5	60	Ring	180	0.0877
72	4.50	50	0.5	80	Ring	180	0.0834
78	4.50	50	0.5	80	Ring	180	0.0766
72	4.75	50	0.5	80	Ring	180	0.0777
78	4.75	50	0.5	80	Ring	180	0.0821

[a] Ratio of wash water flow to skim milk flow into the process.

[b] Samples subjected to dual drying were first dried in a pilot scale ring drier at the first inlet temperature and then dried further in a laboratory scale Glatt fluidised bed drier at the second inlet temperature.

[c] EMC was determined by moisture adsorption for three samples at a_w=0.432 and 30°C. The mean of the three determinations is given.

polar sites, and on the space inside the solid to form water multilayers. The latter two factors are both sterically controlled and would depend on the porosity of the casein solid. It seems likely that the effect of casein drying method on moisture sorption is related mainly to the steric exclusion of water. More severe drying conditions produce lower volume, less porous casein with less space for multilayer formation and binding of water to polar sites.

Table 4.7. Effect of drying conditions on EMC for mineral acid casein[a].

Drying Conditions	Sorption Conditions	EMC[b] (kg water/kg DS)
Never dried	Desorption, 27°C	0.150, 0.141
Freeze dried	Adsorption, 27°C	0.120
Ring/Glatt, 150/50°C	Adsorption, 30°C	0.090[c]
Ring/Glatt, 220/70°C	"	0.088[c]
Ring, 150°C	"	0.086[c]
Ring, 180°C	"	0.081[d]
Ring, 220°C	"	0.081[c]

a Data from Figure 4.4 and Table 4.6.

b Determined at a_w=0.432.

c Mean of four values from Table 4.6.

d Mean of eight values from Table 4.6.

CHAPTER 5
TUNNEL DRYING OF CASEIN CURD

5.1. PRELIMINARY EXPERIMENTS

5.1.1. Reproducibility of Drying Rates

Five batches of laboratory mineral acid casein curd were made at a precipitation pH of 4.6 using the standard conditions in Section 3.1.1. The resulting curd samples had whey pH ranging from 4.55 to 4.65 which also resulted in different initial moisture contents.
The tunnel drier (described in Section 3.2.1) was stabilized for one hour at the standard drying conditions (Section 3.3.2).

After 5 drying runs at the standard conditions the drying rates were compared but were not found to be reproducible. It was hypothesized that the sample initial moisture content needed to be approximately constant in order to have consistent results because drying rates varied with moisture content of the curd.

5.1.2. Determination of Storage Method for Casein Curd

Because different curd initial moisture contents appeared to result in different drying rates, the reproducibility of the tunnel drying method had to be tested on the same batch of casein. As each drying run took three hours and only 4 drying runs could be carried out in one day, a suitable method was required for storing the curd which did not alter the drying characteristics.

Standard mineral acid casein curd was prepared as before. A rapid method for determining the initial moisture content of the curd was performed using the microwave oven (Section 3.3.2.1). This method was not very accurate but was good enough to obtain the approximate initial moisture content of the samples. The total amount of curd which contained approximately 100 grams of dry solids could then be calculated. Three methods of curd storage were considered.

Method A. At the end of the third (final) wash the freshly made curd was divided into two parts. The first half of the curd was dried in a tunnel drier using the standard drying conditions. The second half was kept in a container fully covered with water and stored in a cool store (1-3^{o}C) overnight. The following day the curd was taken out of the container and washed for 5 minutes in 35^{o}C water to simulate the last stage of making fresh curd in the laboratory. The curd was dried at the same drying conditions as for the first portion of the curd. This method was unsuccessful because the physical structure of the curd changed from firm to mushy curd after storing it in the container of water. The drying curve had shifted significantly away from that of the freshly made curd.

Method B. It was hypothesized that the water used in storing the curd might have caused the change in structure of the curd. So at the end of the third wash half of the freshly made curd was pressed hard by hand and packed in a poly-nylon bag and stored in the cool store while the remaining half was dried as in Method A. The following day the stored curd was washed for 5 minutes at 35^{o}C and dried. This method was still unsuccessful because the physical structure of the curd changed from firm to soft curd. Also the drying curve shifted away from that of the freshly made curd.

Method C. It was hypothesized further that maybe the duration and temperature of storing might be causing the change in structure. Again at the end of the third wash half of the curd was pressed hard by hand and packed in a poly-nylon bag and placed on a bench at room temperature (23-25^{o}C) while the other half was dried immediately. At the end of the drying run of the freshly made casein curd, the stored curd was dried under the same drying conditions. It was found that this method did not change the drying characteristics of the curd. Figure 5.1 shows the drying rate curves (dM/dt versus M) of the freshly made and stored curds. As shown by the plots, the two samples had almost identical results. The results also show that the drying rate curve for casein curd dried in a tunnel drier consists of a constant rate period (CRP) and one or more falling rate periods (FRP).

5.1.3. Effect of Initial Moisture Content on Drying Rates

Four drying experiments were conducted on casein curd with initial moisture contents ranging from 1.46 (59.3% w.b.) to 3.02 kg water/kg dry solids (75.1% w.b.). It was necessary to make two batches of fresh curd with half of each batch stored using Method C to avoid variability of sample for each drying run. Figure 5.2 shows the drying rate curves of the casein curd samples with different initial moisture contents. Not all the data points are shown on the drying rate curves.

The results suggest that as the initial MC decreased the drying rate in the CRP increased. However, the CRP drying rates of the two lower moisture samples were not significantly different. The results further show that as the initial MC decreased the

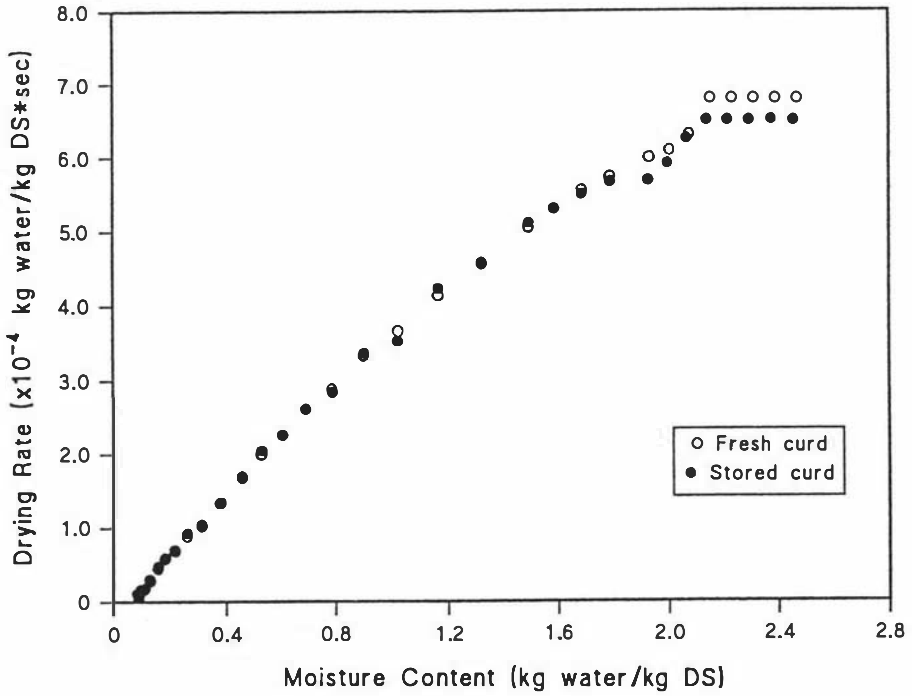


Figure 5.1. Drying rate against moisture content (drying rate curve) of fresh and stored casein curd made using standard conditions and dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

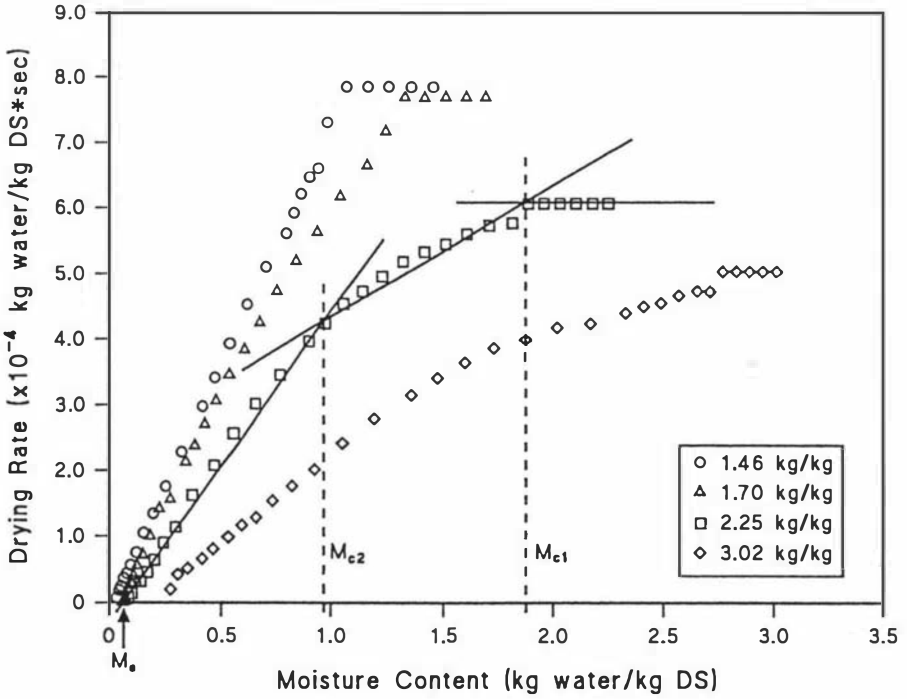


Figure 5.2. Drying rate curves of casein curd (standard conditions) with different initial moisture contents dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

drying rate in the FRP increased.

Drying carrot cubes with different initial water contents in a tunnel drier at $60^{o}C$ also resulted in higher drying rates for lower moisture samples (Bimbenet *et al.*, 1985). However, they did not observe a constant rate period for any of the samples.

The higher drying rates of the low initial moisture samples might be attributed to the different surface characteristics of this curd. The lower moisture samples would probably have a rougher surface leading to a greater surface area and more turbulence across the drying surface resulting in higher drying rates. In contrast, with the high initial moisture samples the surface moisture probably tended to fill the voids and surface hollows between the particles. Hence the drying surface area was reduced to a fairly flat, wet surface. It was also observed that the high moisture samples case hardened easily. As a result, the drying rates in both periods decreased significantly and the critical moisture contents were much higher.

The drying data were analysed using the mathematical modelling procedure outlined in Section 2.2.2. Table 5.1 summarizes the important results. The results indicated that the three high moisture samples had two falling rate periods (denoted by two FRP drying coefficients). As a result, the three high moisture samples had two critical moisture contents. The critical moisture content for each drying run was obtained from the intersections of the modelled linear drying stages on the drying rate curves as shown for the 2.25 kg water/kg dry solids sample (Figure 5.2). The experimental drying curve and the drying curve fitted using the mathematical model are shown in Figure 5.3. The plots show that the mathematical model described the drying curve satisfactorily. The lowest moisture sample had only one FRP and hence one critical MC. As the initial MC of the samples decreased the critical MCs and the final apparent EMCs also decreased.

These results showed that it is necessary to have the same initial moisture contents in order to achieve consistent drying rates between samples in a tunnel drier.

5.2. DRYING RATES OF CASEIN CURD AT STANDARD CONDITIONS

5.2.1. Drying Rate Curves

Drying rate curves of six samples made at standard manufacturing and drying conditions (Section 3.3.2) are shown in Figure 5.4. There seems to be some variation in the drying rates even with all the samples made at exactly the same conditions and

Table 5.1. Effect of initial casein moisture content on drying rate curve parameters.
Manufacturing conditions: laboratory mineral acid casein curd, standard conditions, whey pH=4.59.
Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Initial MC (kg water/ kg DS)	CRP drying Rate ($\times10^{-4}$ kg water/ kg DS*sec)	FRP Drying Coefficient ($\times10^{-4}$ sec^{-1})		Critical MC (kg water/kg DS)		Final Apparent EMC (kg water/kg DS)
		First	Second	First	Second	
1.46	7.85	7.63	-----	1.07	----	0.02
1.70	7.69	4.98	6.80	1.36	0.50	0.04
2.25	6.07	1.70	4.99	1.87	0.95	0.07
3.02	5.03	1.00	2.52	2.97	1.61	0.14

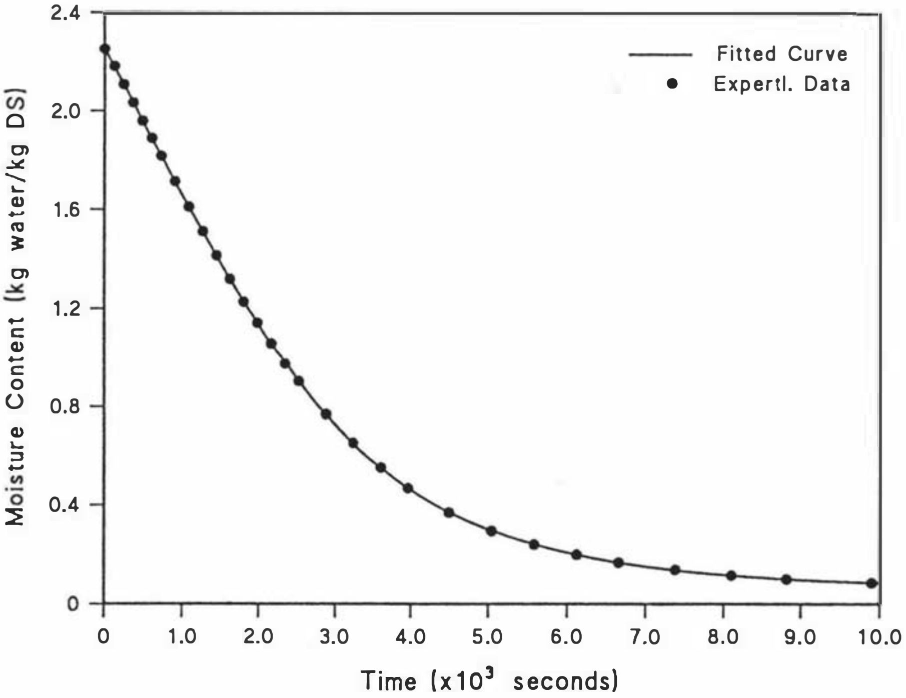


Figure 5.3. Moisture content against time (drying curve) of casein curd (standard conditions) with an initial moisture content of 2.25 kg water/kg DS dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

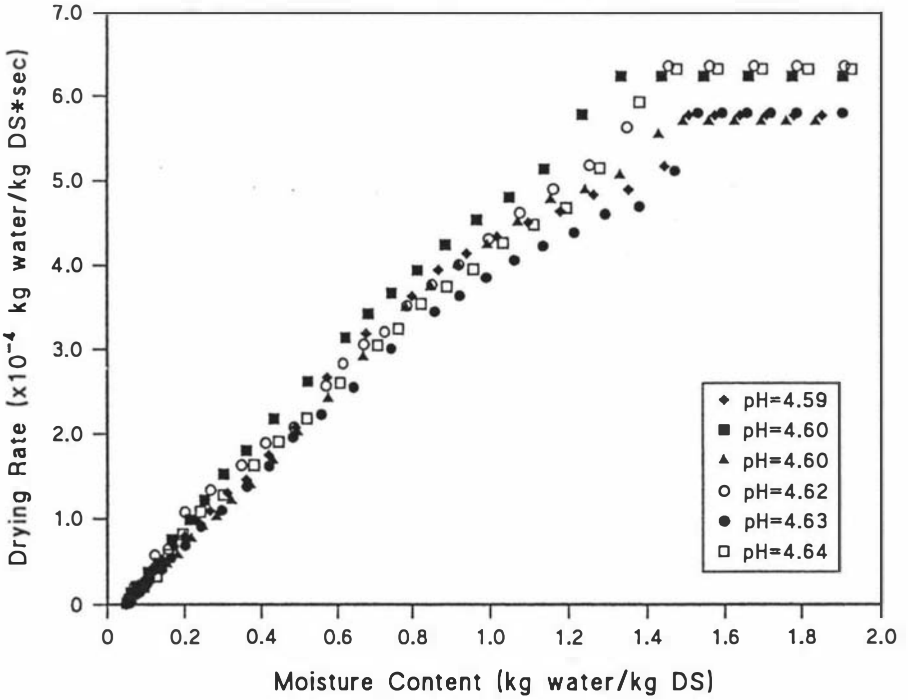


Figure 5.4. Drying rate curves of casein curd made using the standard conditions and dried in a tunnel drier at a DBT of 80°C, air velocity of 5.0 m/s and at ambient humidity (solid symbols indicate different bag of skim milk powder used).

with approximately the same initial moisture content.

The drying data were analysed using the same modelling procedure as in Section 5.1.3. The mean and 95% confidence interval of the CRP drying rate of the six samples was $(6.03 \pm 0.32) \times 10^{-4}$ kg water/(kg dry solids*second) (Table 5.2). The drying rate curves consisted of a CRP and two FRPs.

The differences in the drying rate curves may be caused by slight variations in the casein manufacturing procedures (e.g. degree of turbulence during mixing), in the casein packing on the drying tray or in other drying parameters.

These results will be used to assess the significance of the variations in the drying rates of casein curd with different precipitation pH, precipitation temperature and hot wash temperature.

5.2.2. Theoretical Considerations

Constant Rate Period Drying Rate. The CRP drying rates of samples dried in a tunnel drier can also be calculated from heat transfer considerations (Section 2.2.2). Appendix 5.1 shows a sample calculation for the predicted drying rate using this approach.

Table 5.3 summarizes the results of these calculations. The results show that the drying rates obtained from curve fitting were very close to those from the calculations. Considering that the drying surface area and the heat transfer coefficient were just estimates, the curve fitting procedure is giving similar results to those predicted by simple theory.

Equilibrium Moisture Content. The EMCs of the different casein curds can be obtained from the drying curves, as well as by using the desorption isotherm equation (Section 4.1.2). However, the desorption isotherm equation can only predict the EMC for laboratory mineral acid casein curd prepared under standard conditions. Hence a comparison can only be made for the six runs at standard conditions.

A sample calculation using the desorption isotherm equation to predict the EMC is shown in Appendix 5.2. EMCs calculated by the two methods are compared in Table 5.4. The predicted EMCs using the drying curve were usually higher by 0.010 kg water/kg dry solids than the experimentally determined EMCs derived from the desorption isotherm equation. However, the desorption isotherms obtained did not

Table 5.2. Effect of different batches on drying rate curve parameters.
Manufacturing conditions: laboratory mineral acid casein curd, standard conditions.
Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Sample Whey pH	CRP drying Rate ($x10^{-4}$ kg water/kg DS*sec)	FRP Drying Coefficient ($x10^{-4}$ sec^{-1})		Critical MC (kg water/kg DS)		Final Apparent EMC (kg water/kg DS)
		First	Second	First	Second	
4.62	6.36	4.05	5.71	1.51	0.39	0.040
4.64	6.32	4.07	5.01	1.55	0.36	0.045
4.63	5.80	3.30	4.44	1.60	0.51	0.040
4.60	6.24	4.31	5.55	1.43	0.50	0.040
4.60	5.70	3.93	4.60	1.46	0.44	0.041
4.59	5.77	3.92	5.13	1.45	0.30	0.035
Mean with 95% confidence interval						
4.61±0.02	6.03±0.32	3.93±0.36	5.07±0.52	1.50±0.07	0.42±0.09	0.040±0.003

Table 5.3. Comparison of the CRP drying rates from different methods.
Manufacturing conditions: laboratory mineral acid casein curd, standard conditions, different batches.
Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Sample Whey pH	CRP Drying Rate ($x10^{-4}$ kg water/kg DS*sec)	
	Mathematical Model	Heat Transfer Approach
4.62	6.36	6.09
4.64	6.32	6.00
4.63	5.80	5.75
4.60	6.24	5.94
4.60	5.70	5.57
4.59	5.77	6.00
Mean with 95% confidence interval	6.03±0.32	5.89±0.20

Table 5.4. Comparison of the EMCs from different methods.
Manufacturing conditions: laboratory mineral acid casein curd, standard conditions, different batches.
Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Sample Whey pH	Equilibrium Moisture Content (kg water/kg DS)	
	Mathematical Model	Isotherm Equation
4.62	0.040	0.025
4.64	0.045	0.030
4.63	0.040	0.032
4.60	0.040	0.030
4.60	0.041	0.034
4.59	0.035	0.027
Mean with 95% confidence interval	0.040 ± 0.003	0.030 ± 0.003

cover a_w below 0.10 and hence the EMCs were determined by extrapolation. Therefore the EMC values obtained from the two methods may not be significantly different. The differences in the predicted EMCs using the desorption isotherm equation arise from variations in the humidity of the room and hence in the ERH of the hot air used for drying.

This suggests that the EMCs of casein curd prepared under different conditions, e.g. different pH, can probably be estimated from the drying curve without doing the desorption isotherm determination.

5.3. EFFECT OF CASEIN MANUFACTURING CONDITIONS ON DRYING RATES

In the manufacture of mineral acid casein important variables such as precipitation pH, precipitation temperature, hot wash temperature and degree of plasticisation can affect the drying rates of casein curd. Knowledge of how these variables may influence drying rates may lead to improved efficiency and control of the casein making process.

5.3.1. Precipitation pH

Six drying experiments were conducted on freshly made curd using the standard procedure with different precipitation pH values ranging from 4.0 to 5.0. Figure 5.5 shows the effect of precipitation pH on the drying rate curves of casein curd.

The high pH samples generally dried more slowly than the low pH samples. The results of analyses using the mathematical modelling procedure are shown in Table 5.5. The mean and 95% confidence interval of CRP drying rates of all the runs was $(6.09 \pm 0.29) \times 10^{-4}$ kg water/(kg dry solids*second). The CRP drying rates were not significantly influenced by pH since variation in CRP drying rates for these samples was the same as that found for six samples made at standard conditions (Table 5.2). The results indicated that the drying rates in the first FRP at pH ≤ 4.3 and at pH of 4.95 were significantly different from the samples with a pH range from 4.52 to 4.75. The two higher pH samples have only one falling rate period as compared with the other samples which have two falling rate periods. The first critical moisture content increased with increasing sample pH. However, it seemed that the second critical moisture contents were similar for all samples.

Jablonka and Munro (1985) reported that for batch precipitated mineral acid casein, as precipitation pH increased the curd particle size and calcium content increased. The

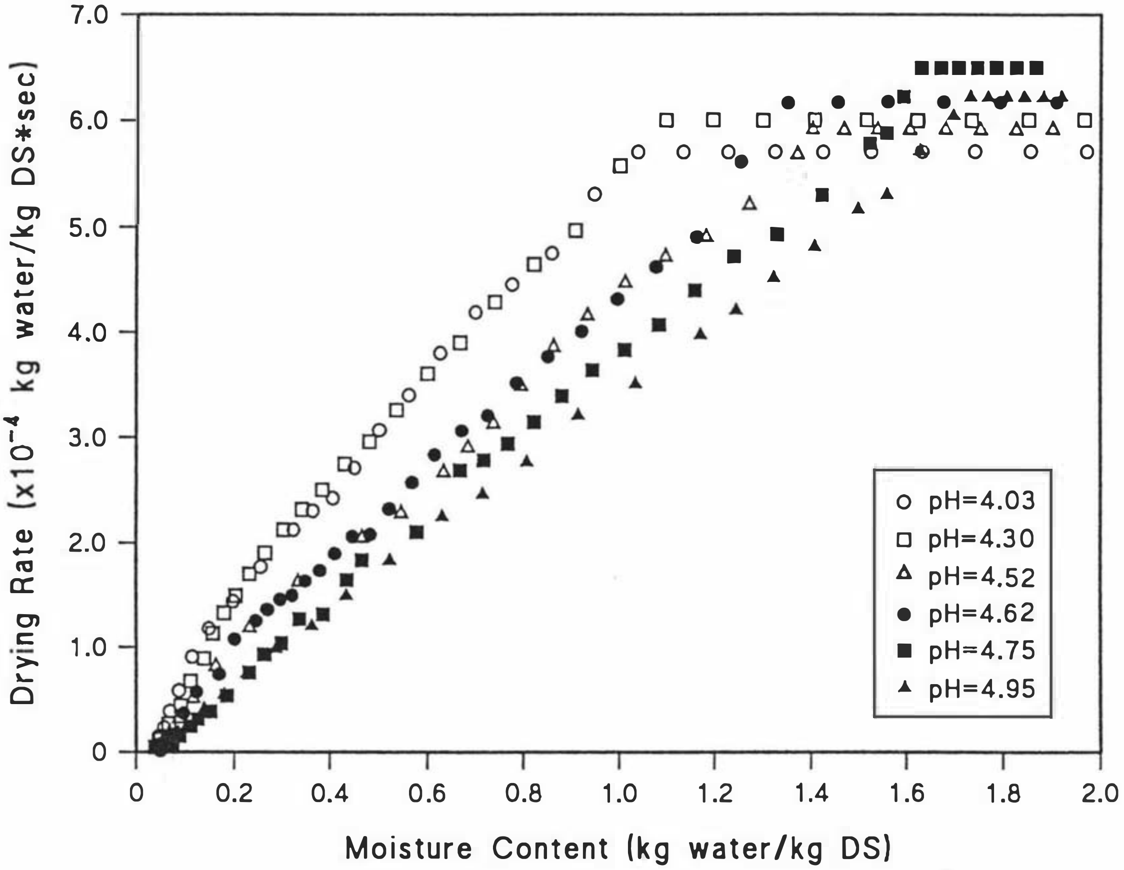


Figure 5.5. Drying rate curves of casein curd with different precipitation pH dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

Table 5.5. Effect of precipitation pH on drying rate curve parameters of laboratory made mineral acid casein curd.
Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Sample Whey pH	CRP drying Rate ($x10^{-4}$ kg water/ kg DS*sec)	FRP Drying Coefficient ($x10^{-4}$ sec^{-1})		Critical MC (kg water/kg DS)		Final Apparent EMC (kg water/ kg DS)
		First	Second	First	Second	
4.03	5.71	4.98	10.17	1.05	0.18	0.031
4.30	6.00	5.00	8.26	1.10	0.20	0.034
4.52	5.91	3.98	6.15	1.43	0.21	0.036
4.62	6.17	4.05	5.50	1.41	0.20	0.039
4.75	6.50	4.03	----	1.64	----	0.049
4.95	6.22	3.60	----	1.74	----	0.030
Mean with 95% confidence interval						
	6.09±0.29	4.27±0.61				0.037±0.007

high pH samples often looked stringy and plastic whereas the low pH curd was soft and crumbly. During drying the high pH samples were sticky when exposed to hot air which resulted in fusion of curd particles at the outset of drying. This behaviour may have hastened case hardening of the matted curd resulting in restricted diffusion of moisture through the surface. This is probably why the end of the constant rate period started much earlier and the drying rate was slower in the falling rate period for the high pH samples. It is also possible that the presence of high calcium concentrations in the high pH curd may have contributed to stickiness of these samples.

5.3.2. Precipitation Temperature

Three drying experiments were conducted on freshly made curd using the standard procedure but with different precipitation temperatures (35, 45 and 60°C). Figure 5.6 shows the drying rate curves of the three samples together with those done at standard conditions (Figure 5.4). The drying rate curve of the 60°C sample was the highest followed by those of the 35°C, 45°C and 53°C samples, respectively. It seems that the effect of precipitation temperature on the drying rates of casein curd was not significant since there was no definite trend in the results, and the variation between the three runs was small. Appendix 5.3 shows the effect of precipitation temperature on the drying rate curve parameters.

5.3.3. Hot Wash Temperature

Two drying experiments were conducted on freshly made curd using the standard procedure but with different hot wash temperatures (55°C and 95°C). A plot of the drying rates against moisture content of the two samples compared with those done at standard conditions (Figure 5.4) is presented in Figure 5.7. The results show that the hot wash temperature has no significant effect on the drying rates of the casein curd. The drying rate curves of the two samples fall within the spread of data for the six standard samples. Appendix 5.4 summarizes the important drying rate curve parameters for the effect of hot wash temperature.

5.3.4. Degree of Plasticization

Three drying experiments were carried out on casein curd obtained from the NZDRI pilot plant at different dewatering temperatures (Section 3.1.2). It was necessary to dewater the pilot plant casein curd in an Alfa Laval decanter in order to get different degrees of plasticization.

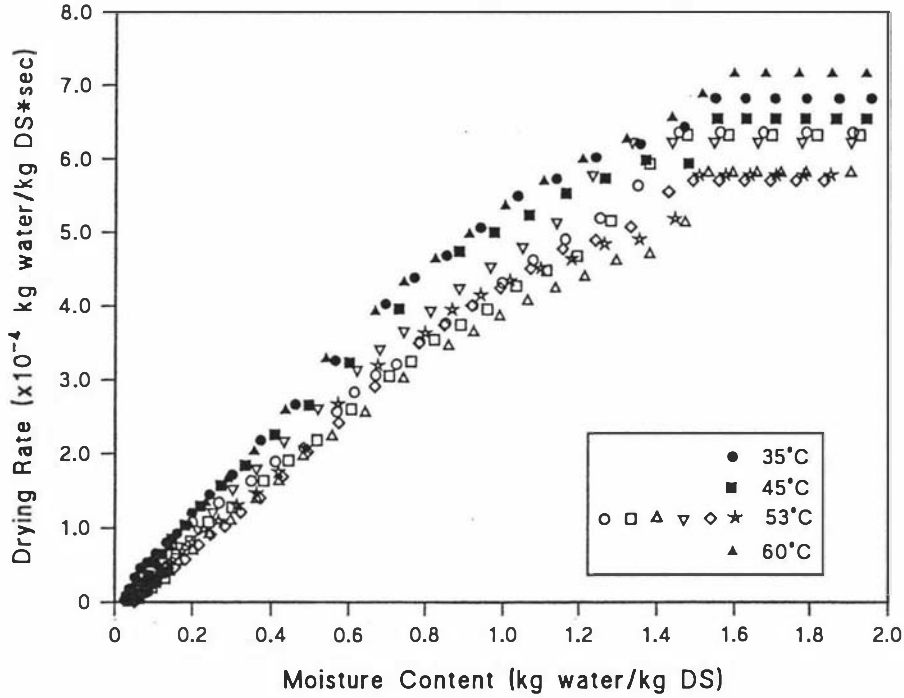


Figure 5.6. Drying rate curves of casein curd with different precipitation temperatures dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

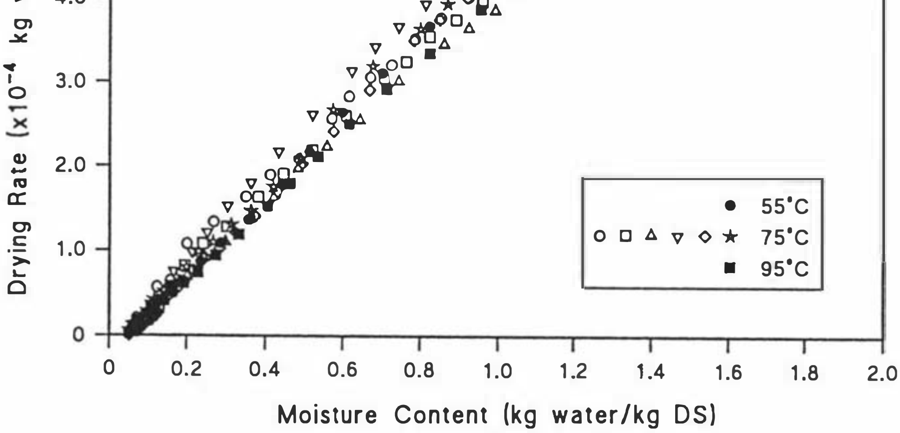


Figure 5.7. Drying rate curves of casein curd with different hot wash temperatures dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

Figure 5.8 shows the drying rate curves of the pilot plant samples. The results showed that the two plasticized samples (high dewatering temperatures) gave higher drying rates than the standard pilot plant sample. The CRP drying rates of the the two plasticized samples are similar to those obtained from the laboratory samples (Section 5.3.1). This may be partly because their initial moisture contents were adjusted to the higher moisture of the standard pilot plant sample, so that the initial samples contained some free water. The standard pilot plant sample (39°C dewatering temperature) had a very low CRP drying rate compared to other samples, even laboratory curd samples. The low CRP drying rate may be due to the packing density of the samples. The standard pilot plant sample had very fine particles which resulted in dense packing in the tray with less air spaces between particles. The dense packing of the particles exposed less overall drying area which may partly explain the lower CRP drying rates for standard pilot plant samples. The two plasticized samples had very high drying rates in the FRP compared with laboratory casein curd, and all three pilot plant samples had much lower critical moisture contents than laboratory curd (Section 5.3.1). The same trends were apparent in a duplicate experiment using a different batch of curd.

The results were quite surprising since the plasticized samples were expected to have lower drying rates because of their less porous appearance and case hardening due to plasticization. It was visually observed however, that the plasticized curd lumps were only plasticized on the outside. When the lumps were broken up before drying, the particles showed greater porosity on the newly broken up surfaces. The plasticization of the curd samples may had resulted in a more rigid structure which did not shrink as much on drying and this lack of shrinkage may have delayed the sealing of the surface. This would result in a more porous structure during the falling rate period which would increase moisture diffusion rates.

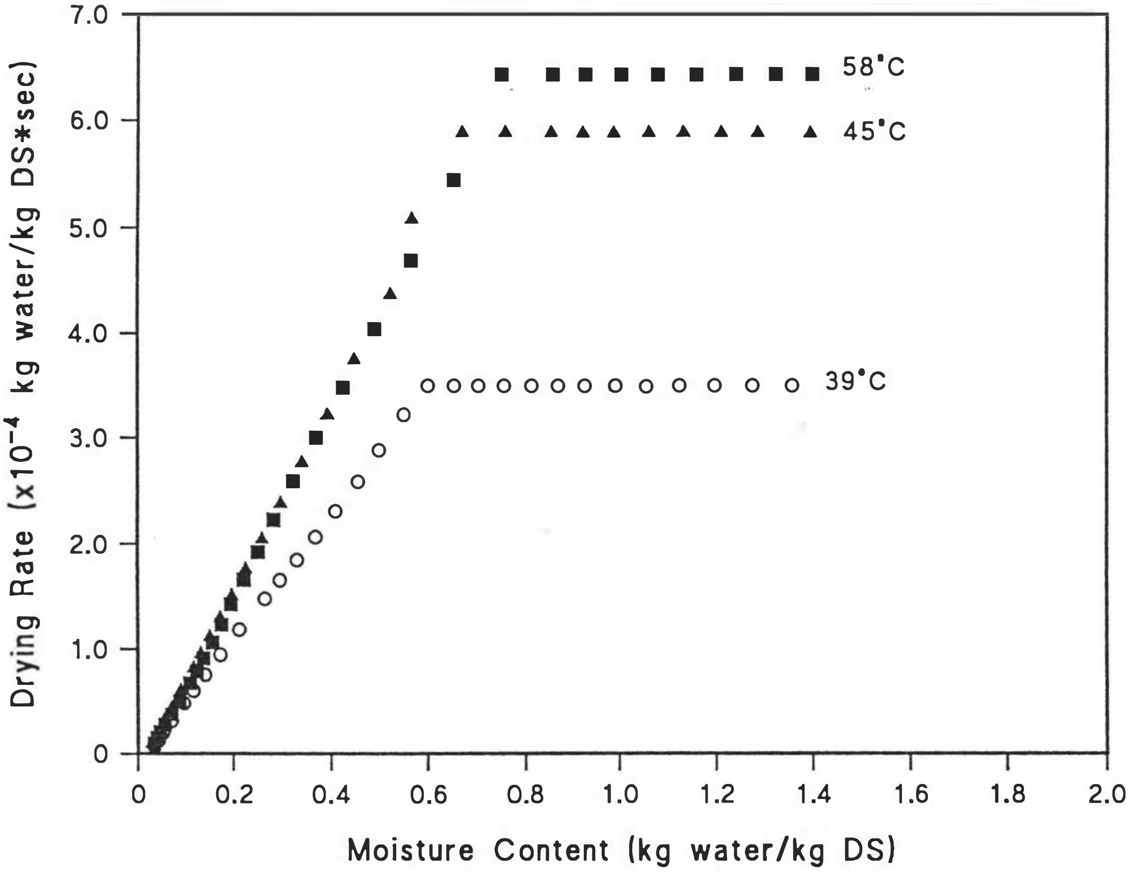


Figure 5.8. Drying rate curves of casein curd (pilot plant) with different dewatering temperatures dried in a tunnel drier at a DBT of 80°C, air velocity of 5 m/s and at ambient humidity.

CHAPTER 6
FLUIDIZED BED DRYING OF CASEIN CURD

6.1. PRELIMINARY EXPERIMENTS

6.1.1. Drying of Laboratory Casein Curd

About 3 kg of laboratory standard mineral acid casein curd was placed in a plastic bag. The fluidized bed drier was set at an air inlet temperature of $81^{\circ}C$, an air velocity of 2.0 m/s and at ambient humidity. After the drier reached steady state, the vibrator was turned on, the air flow was turned off and the bag of casein curd was emptied into the drier. The filter bag was put back and the air flow resumed. The run was discontinued after several minutes because the sample caked and did not fluidize. It was suspected that the high moisture content of the curd hastened the caking process.

A second batch of casein curd was made using the standard procedure. After screening, the curd was pressed hard by hand to get rid of surface water. The curd was again subjected to the same drying conditions as before. The sample still caked after several minutes of drying and hence was abandoned.

Due to the large amount of curd needed for each drying run (to produce 3 kg of curd about 45 litres of reconstituted skim milk was used), the use of laboratory made casein curd was discontinued.

6.1.2. Drying of Pilot Plant Casein Curd

About 3 kg of dewatered mineral acid casein curd was obtained from the NZDRI pilot plant. The casein curd was dried in the fluidized bed drier as before. The sample also caked after several minutes in the drier. It was hypothesized that the hot drying chamber caused the caking of the curd when it was put in at the start of drying.

A second batch of mineral acid casein curd (3 kg) was put into the drier with the vibrator on and the air flow was turned on. Enough heaters to get the desired air inlet temperature were also turned on. It took about 5 minutes for the drier to reach the inlet temperature of $81^{\circ}C$ at an air velocity of 2.0 m/s. The casein curd fluidized satisfactorily. Samples were taken periodically from the drier using the sampler and sealed in plastic bags until moisture content determination. The sample remained fluidized until the end of drying.

Analyses of the drying data (using the same mathematical model as used for the tunnel drying data) revealed that the casein curd had a long constant rate period. The falling rate period did not start until a critical moisture content of 0.4 kg water/kg dry solids. Hence, this procedure was adopted as the standard procedure for drying casein curd in the fluidized bed drier.

The earlier study used 3 kg of casein curd and the total amount of curd withdrawn was about 300 g. The sample withdrawn represents about 10% of the casein put into the drier. It was anticipated that this large amount of sample might affect the drying rate.

A third batch of 5 kg mineral acid casein was subjected to the same drying conditions. This drying run produced a similar result with a long constant rate period until a critical moisture content of about 0.5 kg water/kg dry solids and one falling rate period.

In the last two drying runs, the casein fluidization appeared to be very turbulent. This suggested that the air flow used was too high. Three 5 kg lots of casein were dried at 81°C and air velocities of 1.4, 1.6 and 1.8 m/s. It was observed that the drying run with 1.4 m/s air velocity did not fluidize at first but after it had partly dried it did fluidize. This meant there was an unsteady state period which was not desirable for experimental purposes. The drying run with at 1.8 m/s had very good fluidization at the start of drying but was very turbulent later. It seemed that the drying run at 1.6 m/s gave the best fluidization. The 1.6 m/s air velocity was therefore adopted for the succeeding drying experiments.

6.1.3. Effect of Humidity on Drying Rates

The inlet air relative humidity could not be accurately controlled in the fluidized bed drier. Over several runs the inlet air humidity varied from 0.006 to 0.0118 kg/kg dry air, which was mainly due to daily variation in ambient conditions. As there was a possibility that the changes in air humidity could influence the drying rate, drying was studied at different humidities but otherwise standard conditions. About 10 kg of dewatered casein curd was divided into two 5 kg lots. The first lot was dried at an air inlet temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity (0.0066 kg water/kg dry air). The second half was also dried using the same conditions but steam was introduced prior to the plenum chamber thereby increasing the humidity of the air to 0.0150 kg water/kg dry air.

Figure 6.1 shows the drying rate curves for pilot plant casein curd with different air humidity. The drying data were analysed using the mathematical model used for the tunnel drying data. The results indicate that an increase in humidity seems to cause a slight decrease in the CRP drying rates but has very little effect in the falling rate period.

When the humidity of the air increases, the humidity driving force between the air and the wet solid decreases thereby lowering the drying rates during the constant rate period (Williams-Gardner, 1971). The results obtained coincided with the findings of Haertling (1980) on drying pumice concrete (a hygroscopic material) at different humidities. Bimbenet *et al.* (1985) also reported that lower humidity air gave higher drying rates at the beginning of drying for carrots and potatoes even though both products had no CRP. From the results in Figure 6.1, small changes of ambient air humidity should not significantly affect the drying rate of casein curd.

6.1.4. Trials of the Rotronics Humidity Probe in the Drier Exhaust

In the early stages of the fluidized bed drying study, a Rotronics humidity probe was used to monitor the changes in the relative humidity of the outlet air during drying. The probe also monitored the outlet air temperature. The potential of the probe to follow the changes during drying was examined.

The humidity probe was calibrated as specified from the Rotronics manual at relative humidities of 30% and 80% and ambient temperature (20-25°C). Ampoules of unsaturated lithium chloride from Rotronics were used in the calibration cell. The minimum and maximum temperature were also calibrated.

The Rotronics humidity probe was installed at the top end of the drying chamber. The probe was fitted with an air filter made of a sintered stainless steel cup to prevent contamination from casein fines. Relative humidity readings were monitored using the Molytek potentiometric recorder. Casein curd was dried using the standard conditions. Moisture sampling was also carried out to compare the results with the Rotronics humidity probe.

Results had shown that the probe followed the constant rate period quite well by showing 100% relative humidity during this period. However, the drop in the outlet air relative humidity was 6 to 8 minutes later than the rise in the outlet air temperature (readings from the thermocouple) and the fall in the drying rate (obtained from the moisture sampling).

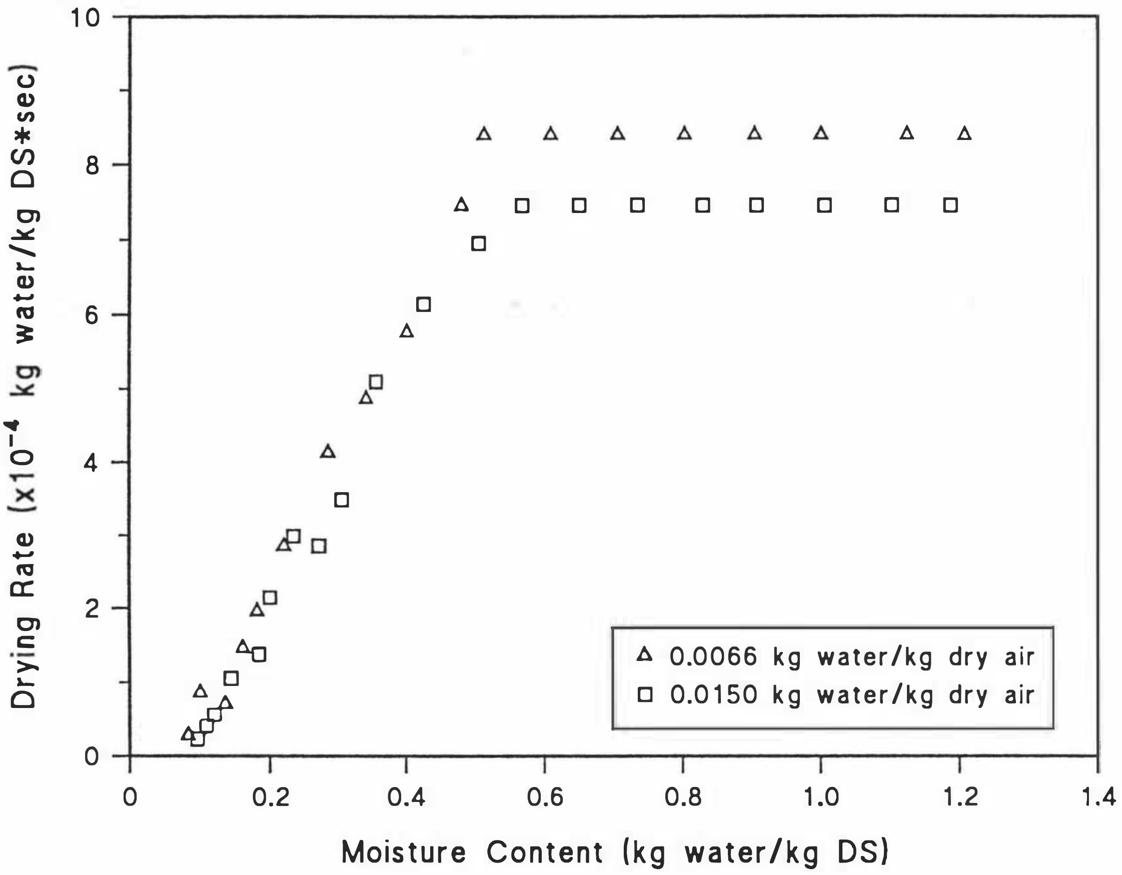


Figure 6.1. Drying rate curves of pilot plant mineral acid casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at different air humidity.

During the drying period, it was observed that the air filter on the probe was quickly covered with casein fines. It was thought that these fines might be causing the delay in the outlet relative humidity change. It was decided therefore to change the air filter on the probe. Several probe filters from Rotronics were tested and were found to be unsuitable for the purpose. Several specially made air filters were also tried and one design gave encouraging results. Figure 6.2 shows the improved air filter used on the Rotronics probe during casein drying.

Several drying runs were conducted using the specially constructed air filter on the Rotronics probe. The results showed that the lag problem encountered during the constant rate period decreased to about 3 or 4 minutes. It was deduced that the lag problem was probably inherent to the probe and was not pursued any further. It was also noticed that the outlet air relative humidity at the end of drying was always above 10%. This was found to be much higher than the expected relative humidity of the air using the psychrometric chart given the initial humidity of the air and the final outlet temperature.

After several more experiments it was found that the Rotronics probe used had a defective temperature compensator which caused the wrong relative humidity readings at the end of drying.

Another Rotronics probe was used and it was found that it could monitor the outlet air relative humidity satisfactorily over the duration of drying. It was found however that the response time of the probe (relative humidity and temperature) was slow and could not keep up with the drying rate changes. Hence the use of the Rotronics probe to monitor the changes during the drying of casein curd was abandoned.

6.1.5. Effect of Storage on Drying Rates

The casein curd used in the fluidized bed drying studies came from either the NZDRI pilot plant (Section 3.1.2) or the Tui Milk Products casein factory (Section 3.1.3). There was a need to find a suitable storage method for casein curd for the following reasons:

a) a limited number of drying runs could be done in one day (3 maximum);
b) the intermittent supply of samples from the pilot plant; and
c) the difficulty in obtaining frequent casein curd samples from the factory because of contamination risks.

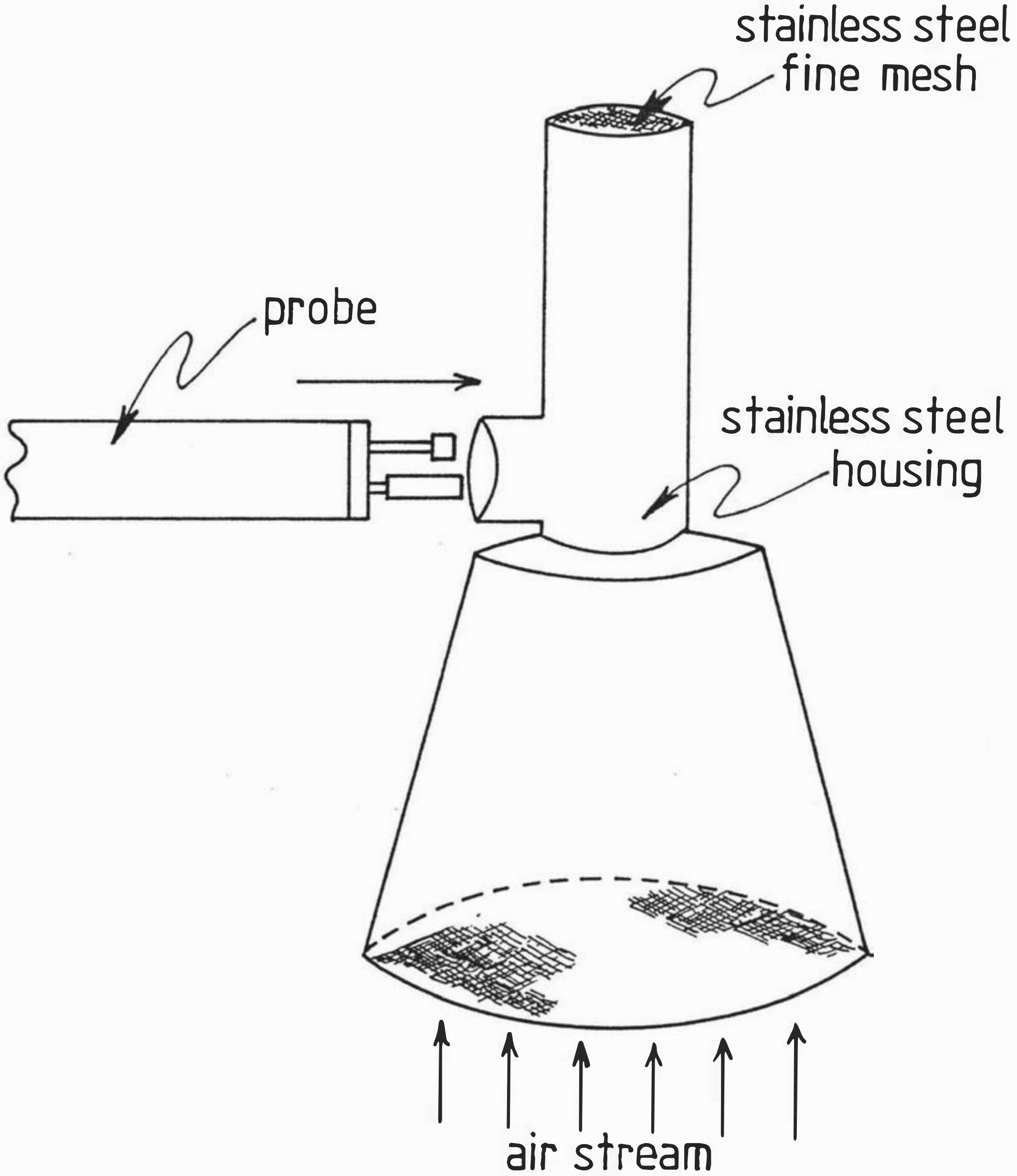


Figure 6.2. Schematic diagram of the air filter used on the Rotronics probe during the fluidized bed drying of casein curd.

Figure 6.3 shows the drying rate curves of two batches of pilot plant casein curd with different storage time in the cool store. The drying data were analysed as before and the results are presented in Table 6.1. The results indicate that the drying rates of casein curd were not affected by up to six days of storage. The results also show that the drying rates of the two batches of casein were not significantly different.

6.2. DRYING RATES OF CASEIN CURD AT STANDARD CONDITIONS

6.2.1. Drying Rate Curves of Pilot Plant Casein Curd

The drying rate curves of five batches of fresh pilot plant casein curd dried at standard conditions (Section 3.2.2) are presented in Figure 6.4. The data suggest that the drying of casein curd consist of a constant rate period (CRP) and only one falling rate period (FRP).

The drying data were analysed using the mathematical model used in the tunnel drying (Table 6.2). The mean CRP drying rate was $(8.06 \pm 0.38) \times 10^{-4}$ kg water/(kg dry solids*second) and the FRP drying coefficient was $(1.90 \pm 0.12) \times 10^{-3}$ second^{-1}.

Figure 6.5 shows the drying curve for one experiment. There is a good agreement between the experimental data points and the line derived from the mathematical model. This suggests that the mathematical model fits the experimental drying curve adequately.

The plots of drying rate, outlet air relative humidity, probe and thermocouple outlet air temperatures, bed temperature and inlet air temperature against time for a representative sample are shown in Figure 6.6. The end of the constant rate period could be determined from the fall in drying rate, from the rapid drop in outlet air RH and from the rapid rise in the outlet air temperature. The bed temperature usually rose ahead of the outlet air temperature because as the casein dried the bed voidage increased resulting in the exposure of the bed thermocouple to the heated air. The drying rate, the outlet air RH and temperature measurements at the end of the constant rate period corresponded reasonably well for most drying runs. However as pointed out earlier, the probe readings lag the drying rate and thermocouple outlet temperature data by about 4 minutes. Majkowski *et al.* (1988) also reported that for fluidized bed drying of casein, the outlet air temperature stayed constant at 30^{O}C for several minutes before increasing using an inlet air temperature of 80^{O}C.

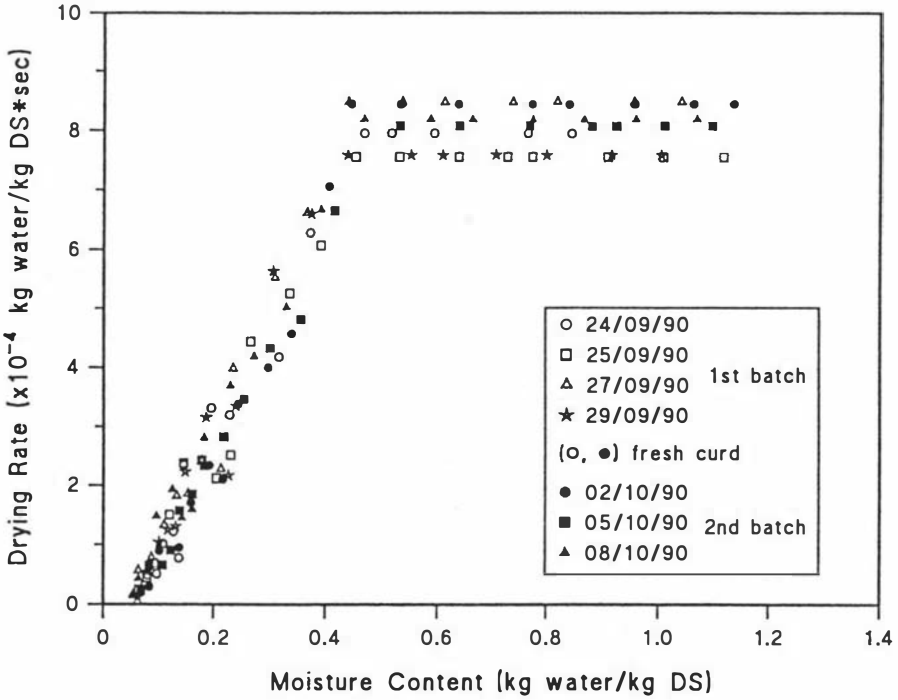


Figure 6.3. Drying rate curves of 2 batches of fresh and stored casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

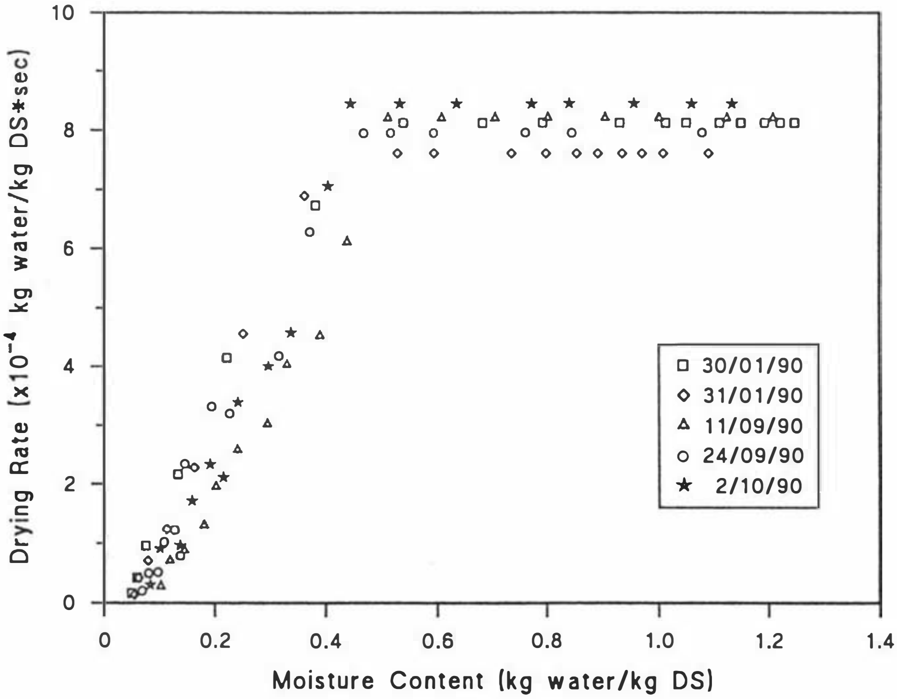


Figure 6.4. Drying rate curves of different batches of casein curd made at constant manufacturing conditions and dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Table 6.1. Drying data for two batches of fresh and stored pilot plant mineral acid casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Date the Sample was Dried	Initial MC (kg water/kg DS)	MC at t=0 (kg water/kg DS)	CRP Drying Rate ($\times 10^{-4}$ kg water/ kg DS*sec)	FRP Drying Coefficient ($\times 10^{-3}$ sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC (kg water/kg DS)
First Batch						
24/09/90[a]	1.297	1.046	7.954	1.920	0.061	0.47
25/09/90	1.314	1.117	7.554	1.933	0.055	0.45
27/09/90	1.320	1.040	8.470	2.031	0.047	0.47
29/09/90	1.317	1.005	7.587	2.000	0.056	0.44
Mean with 95% confidence interval						
	1.31±0.02		7.89±0.68	1.97±0.08	0.055±0.009	0.46±0.02
Second Batch						
02/10/90[a]	1.340	1.135	8.438	1.837	0.070	0.52
05/10/90	1.324	1.096	8.075	1.913	0.062	0.49
08/10/90	1.344	1.068	8.183	1.931	0.047	0.47
Mean with 95% confidence interval						
	1.34±0.03		8.23±0.46	1.90±0.12	0.060±0.029	0.49±0.06
Overall Mean with 95% confidence interval						
	1.32±0.01		8.14±0.34	1.93±0.05	0.057±0.010	0.47±0.03

[a] fresh curd

Table 6.2. Drying data for five batches of fresh pilot plant mineral acid casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81^{o}C, an air velocity of 1.6 m/s and at ambient humidity.

Date the Sample was Obtained	Initial MC	MC at t=0	CRP Drying Rate ($x10^{-4}$ (kg water/ kg DS*sec)	FRP Drying Coefficient ($x10^{-3}$ sec^{-1})	Apparent EMC	Critical MC
	(kg water/kg DS)				(kg water/kg DS)	
30/01/90	1.296	1.248	8.12	2.017	0.038	0.44
31/01/90	1.234	1.092	7.61	1.983	0.048	0.43
11/09/90	1.471	1.209	8.20	1.783	0.089	0.54
24/09/90	1.297	1.046	7.95	1.920	0.061	0.47
02/10/90	1.340	1.135	8.44	1.837	0.070	0.52
Mean with 95% confidence interval	1.33±0.11		8.06±0.38	1.90±0.12	0.061±0.025	0.48±0.06

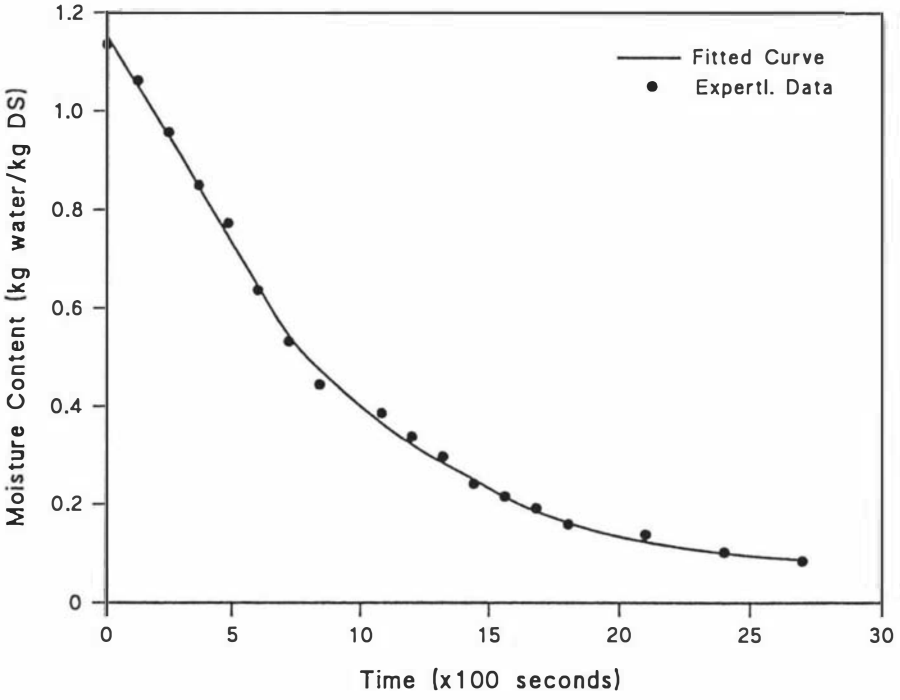


Figure 6.5. Moisture content versus time (drying curve) of casein curd made at standard conditions and dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

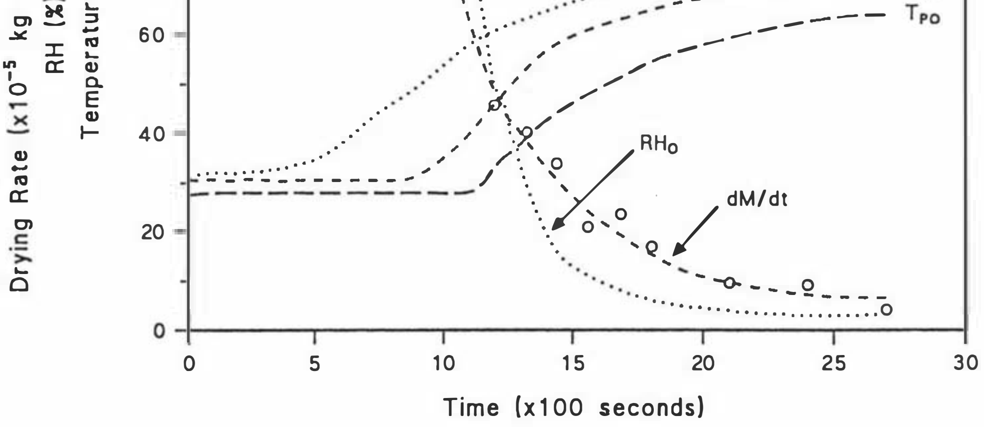


Figure 6.6. Fluidized bed drying of casein curd showing the drying rate (dM/dt), outlet relative humidity (RH_O), probe outlet temperature (T_{PO}), thermocouple outlet temperature (T_{TO}), bed temperature (T_B) and inlet temperature (T_I) over the duration of drying.

Espie *et al.* (1984) also reported the presence of a constant rate period during the drying of different types of pilot plant casein curd using a laboratory fluidized bed drier.

The observed constant rate period for the casein curd was due to the presence of excess unbound moisture within the sample. This period of drying will continue as long as the migration of moisture to the surface at which evaporation is occurring can keep pace with the evaporation taking place at that surface (Williams-Gardner, 1971; Brennan *et al.*, 1976). The falling rate period starts when the rate of moisture movement from within the material to the surface becomes less than the evaporation from the surface. The surface begins to dry out and the rate of drying begins to fall. The surface temperature begins to rise as there is now insufficient evaporative cooling. It continues to do so as drying proceeds, approaching the dry bulb temperature of the air as the material approaches dryness (Brennan *et al.*, 1976).

6.2.2. Comparison with the Tunnel Dried Casein Curd

The fluidized bed drier produced a relatively long constant rate period which continued till the critical moisture content of around 0.5 kg water/kg dry solids was reached. The falling rate period was very well modelled by one straight line. The curd dried in the tunnel drier had only a very short constant rate period which finished at a high critical moisture content of around 1.5 kg water/kg dry solids. Two straight lines were required to adequately model the falling rate period.

The difference in the drying rate curves for the two driers may be attributed to the different air/casein contact regimes in the two driers. In the fluidized bed drier the air flows up through the bed of casein and fluidizes it. The entire surface of all the casein particles is therefore exposed to the drying air, and the moisture diffusion path is short. The constant rate period therefore continues until close to the end of drying. In the tunnel drier the air flows across the surface of a stationary casein sample. The drying surface area is relatively small. The outer surface of the casein dries relatively rapidly and can be seen visually to partially fuse together. It thus develops a hard surface layer which acts as a barrier to further moisture diffusion into the air. The drying rate thus begins to drop relatively soon after the beginning of drying.

6.3. EFFECT OF DRYING CONDITIONS ON DRYING RATES

6.3.1. Air Drying Temperature

Drying Rates of Pilot Plant Casein Curd. From the second batch of casein curd (Figure 6.3), two drying runs were conducted at drying temperatures of 60°C and 126°C while the air velocity was held constant.

The drying rate curves for pilot plant casein curd with different air inlet drying temperatures are presented in Figure 6.7. The plots indicate that in both the constant rate period and falling rate period the drying rates of casein curd increased with an increase in air inlet drying temperature.

Table 6.3 summarizes the analyses of the drying data. The apparent equilibrium moisture content (EMC) decreases with an increase in drying temperature. With an increase in drying temperature the relative humidity of the drying air will also decrease thereby lowering the EMC. The temperature of the curd will increase in the falling rate period as a result of an increase in drying temperature and this will also lower the EMC. The results therefore are consistent with the desorption isotherm studies in Section 4.1.1. The critical moisture contents of the three samples were essentially the same. This perhaps indicates that the casein curd was not affected by the high drying temperature during the constant rate period. This is due to the cooling effect of the evaporating water from the curd during this period. Thus the surface temperature remains close to the wet bulb temperature of the drying air and hence no overheating occurs.

The increase in CRP drying rate with an increase in drying temperature is expected from drying theory (Forrest, 1968; Williams-Gardner, 1971; Karel, 1975; Toledo, 1980; Watson & Harper, 1988). The same observations were also noted by Haertling (1980) in drying pumice concrete, clay brick and burned clay at different inlet air temperatures. During the constant rate period, the rate of evaporation of moisture is proportional to the temperature difference between air and particle surface or wet bulb temperature of the air (Equation 2.1). Hence the higher the air drying temperature the higher the moisture evaporation rate. This means that in casein drying during the constant rate period it is best to use as high an air inlet temperature as possible to increase the drying rate without any danger of overheating the casein curd.

Table 6.3 also shows that the FRP drying coefficient increased with the drying temperature, in line with previous studies (Fornell *et al.*, 1980; Bimbenet *et al.*, 1985; Chiang & Petersen, 1985; Yusheng & Poulsen, 1988; Ajibola, 1989; Diamante & Munro, 1991). During the falling rate period, the rate of moisture diffusion is proportional to the curd surface temperature which is dependent on the drying temperature. Therefore the higher the air drying temperature the higher the moisture

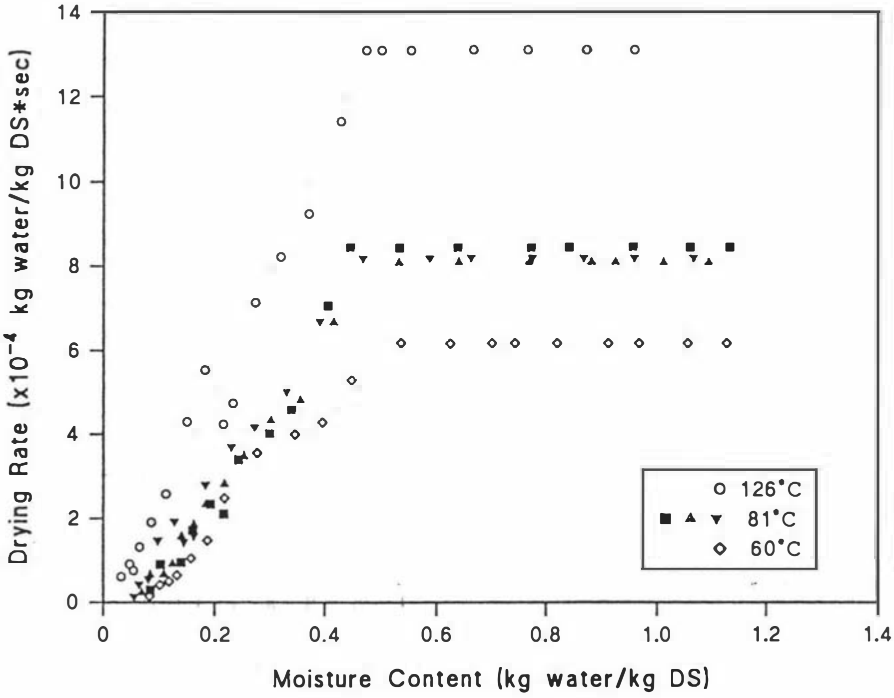


Figure 6.7. Drying rate curves of pilot plant casein curd dried in a fluidized bed drier with different air inlet drying temperatures, an air velocity of 1.6 m/s and at ambient humidity.

Table 6.3. Drying data for pilot plant mineral acid casein curd dried in a fluidized bed drier at different air inlet drying temperatures, an air velocity of 1.6 m/s and at ambient humidity.

Inlet Air Drying Temp. (^oC)	Initial MC (kg water/kg DS)	MC at t=0 (kg water/kg DS)	CRP Drying Rate (kg water/ kg DS*sec)	FRP Drying Coefficient (sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC (kg water/kg DS)
60	1.324	1.128	0.000616	0.001405	0.075	0.51
81	1.350	1.096	0.000818	0.001931	0.047	0.47
126	1.324	0.957	0.001309	0.002637	0.015	0.51

diffusion out of the product. The results suggest that to increase the casein drying rate, the use of a higher drying temperature is advisable even in the the falling rate period. However since the casein curd is no longer sufficiently cooled by evaporative cooling, its temperature can rise significantly as the moisture content drops. This places a practical limit on the temperature in the falling rate period as the results of the experiments on the thermal sensitivity of casein show (Section 10.5).

Drying Rate Curves of Commercial Casein Curd. The effect of drying temperature on the drying rate of commercial lactic casein curd was also studied. Four drying runs were conducted at drying temperatures between 28^{o}C and 132^{o}C, at an air velocity of 1.6 m/s and at ambient humidity.

The results are presented in Figure 6.8 which shows that in both the constant rate period and the falling rate period the drying rates of casein curd increase with an increase in the air inlet temperature.

Drying data is shown in Table 6.4 and show similar trends with temperature for the apparent EMC, critical moisture content, CRP drying rate and the FRP drying coefficient as for the pilot plant samples.

Theoretical Considerations for the Constant Rate Period. From drying theory (Nonhebel & Moss, 1971; Williams-Gardner, 1971; Heldman, 1975; Brennan *et al.*, 1976; Watson & Harper, 1988), it is possible to derive the heat transfer coefficient from the drying rate in the CRP and the drying conditions from Equation 2.1 (Section 2.2.2),

$$A\,R_c = (dM/dt)_c\,W = \frac{h\,A\,(T_a - T_w)}{L} \qquad (2.1)$$

where $(T_a - T_w)$ is best calculated as $(T_a - T_w)_{lm}$ (log mean temperature driving force) because the condition of the air changes significantly in passing from the inlet to the outlet of the drier. Table 6.5 summarizes the relevant data for pilot plant and commercial casein curd samples dried in the fluidized bed drier at different drying temperatures. Figure 6.9 shows an evaporation rate versus temperature driving force plot for the two sets of samples. Appendix 6.1 shows the sample calculations for the data plotted on Figure 6.9. The slopes of the regression lines of the samples equal (h A). The heat transfer coefficient was not obtained because of the difficulty in solving the actual available drying area of casein.

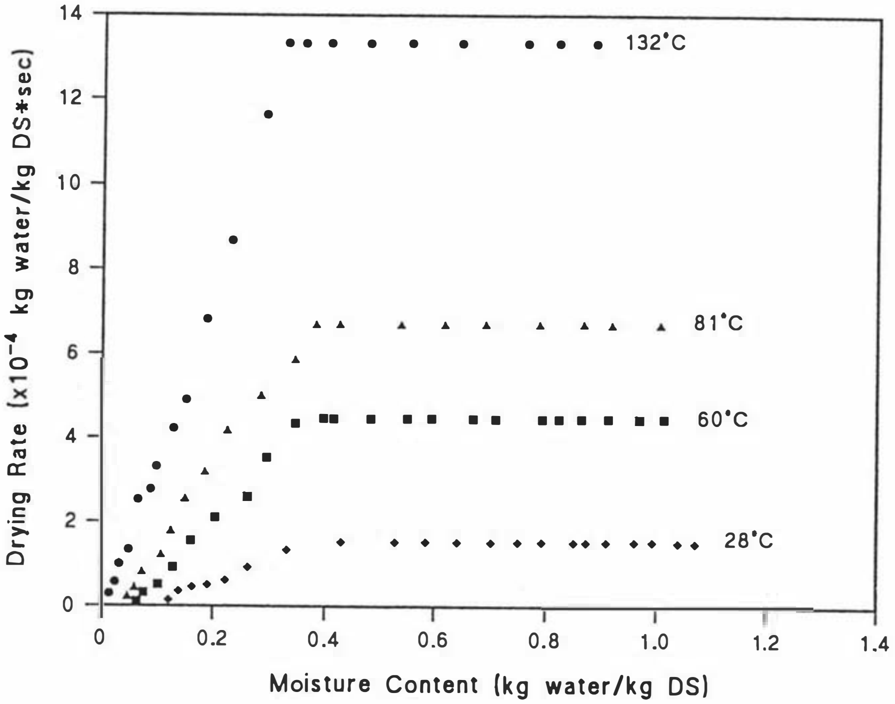


Figure 6.8. Drying rate curves of commercial casein curd dried in a fluidized bed drier with different air inlet drying temperatures, an air velocity of 1.6 m/s and at ambient humidity.

Table 6.4. Drying data for commercial lactic casein curd dried in a fluidized bed drier at different air inlet drying temperature, an air velocity of 1.6 m/s and at ambient humidity.

Inlet Air Drying Temp. (^{o}C)	Initial MC (kg water/kg DS)	MC at t=0 (kg water/kg DS)	CRP Drying Rate (kg water/ kg DS*sec)	FRP Drying Coefficient (sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC (kg water/kg DS)
28	1.189	1.071	0.000153	0.000463	0.073	0.41
60	1.183	1.013	0.000445	0.001390	0.056	0.38
81	1.143	1.005	0.000668	0.002414	0.042	0.32
132	1.154	0.886	0.001332	0.003818	0.009	0.36

Table 6.5. Data for the pilot plant and commercial casein curd samples dried in the fluidized bed drier at different air inlet temperatures (Used to plot Figure 6.9).

Inlet Air Drying Temp. (Ta1) (^oC)	Air Wet Bulb Temp. (Twb) (^oC)	CRP Drying Rate (kg water/ kg DS*sec)	Mass of Dry Solids (kg)	Outlet Air Temp. $(Ta2)^a$ (^oC)	Log Mean Temp. Diff. $(Ta1-Ta2)_{lm}$ (^oC)	Latent Heat of Evap.@ Twb $(KJ/kg)^b$
Pilot Plant Mineral Acid Casein Curd						
60	25.5	0.000616	2.15	27.2	10.8	2440
81	30.0	0.000807	2.15	37.5	22.7	2431
126	37.5	0.001309	2.15	55.9	44.6	2411
Commercial Lactic Casein Curd						
28	19.5	0.000153	2.30	19.3	2.6	2455
60	27.5	0.000445	2.30	34.7	16.8	2436
81	31.0	0.000668	2.40	41.4	25.2	2429
132	38.5	0.001332	2.35	54.7	44.1	2410

a calculated using the heat and mass balance

b from Keenan *et al.* (1969)

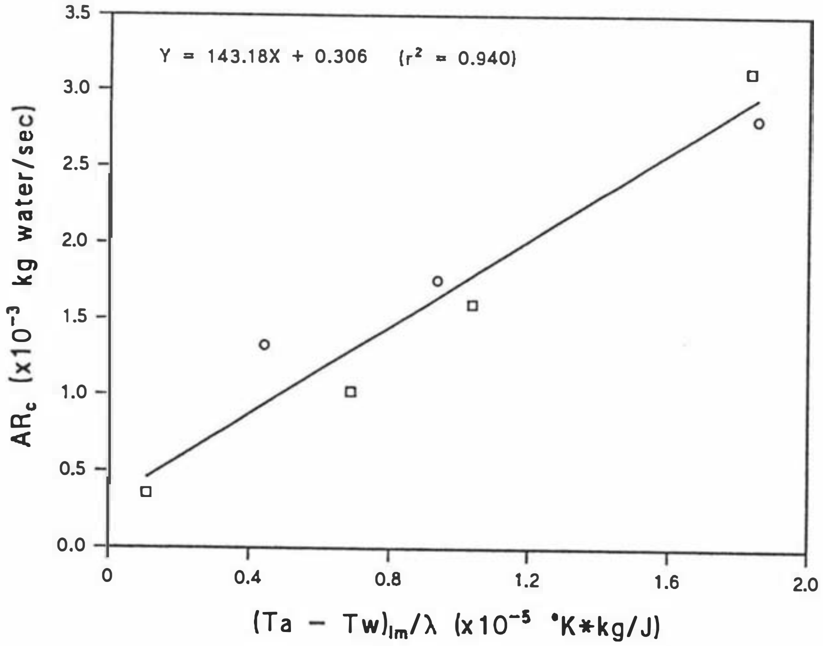


Figure 6.9. Plot of the product of drying area (A) and CRP moisture evaporation rate (R_c) against the ratio of log mean temperature difference $(Ta-Tw)_{lm}$ and latent heat of evaporation of water at Tw (λ) for pilot plant (○) and commercial (□) casein curds dried in a fluidized bed drier at an air velocity of 1.6 m/s and at ambient humidity.

Theoretical Considerations for the Falling Rate Period. Henderson and Pabis (1961) showed that the temperature effect on the FRP drying rate constant (from the exponential equation) for grains followed an Arrhenius type equation. More recently, several investigators also expressed the FRP drying rate constant of different foods as an Arrhenius type equation (Ross & White, 1972; White *et al.*, 1981; Chiang and Petersen, 1985; Verma *et al.*, 1985; Ajibola, 1989).

Plots of the natural logarithm of FRP drying coefficient (ln F) against the reciprocal of drying temperature (1/T) for the pilot plant and commercial casein samples are shown in Figure 6.10. The results indicate that for both samples the FRP drying coefficient could be described by an Arrhenius type equation. The results also show that the commercial casein curd gave a higher slope than the pilot plant sample. However a single regression line can satisfactorily describe all the data points. The 'apparent activation energy' for the FRP drying coefficient of casein was calculated from the slope of the regression to be 17.73 kJ/mole (Appendix 6.2). Table 6.6 presents the 'apparent activation energies' based on the FRP drying coefficients for different biological products which are fairly similar to casein. The value for casein was similar to that of french-fry cut potato but a little lower than those of rice, melon seed, yellow corn and popcorn. The grains probably had a higher activation energy because of the presence of a seedcoat which hindered the diffusion of moisture out of the product.

6.3.2. Air Velocity

Drying Rates of Pilot Plant Casein Curd. The effect of air velocity on the drying rate of pilot plant casein curd was studied. From the second batch of casein curd (Figure 6.3), two drying runs were carried out at air velocities of 1.4 m/s and 1.9 m/s with all other conditions held constant. The average d_{50} for this batch of casein was 2.10 mm.

Figure 6.11 shows the drying rate curves for pilot plant casein curd with different air velocities. The figure indicates that the air velocity affected the drying rates in the constant rate period only. The casein curd dried with an air velocity of 1.4 m/s had an unsteady period which was brought about by insufficient fluidization initially. However, after several minutes the curd had dried sufficiently so that fluidization improved and the drying rate increased. By disregarding the unsteady period, the CRP drying rates for the 1.4 m/s data and the 1.6 m/s data were not significantly different. Using an air velocity of 1.9 m/s the increase in the CRP drying rate was barely more than the upper bound for the mean on the 1.6 m/s data (Table 6.2). The drying rates in the falling rate period were not significantly affected.

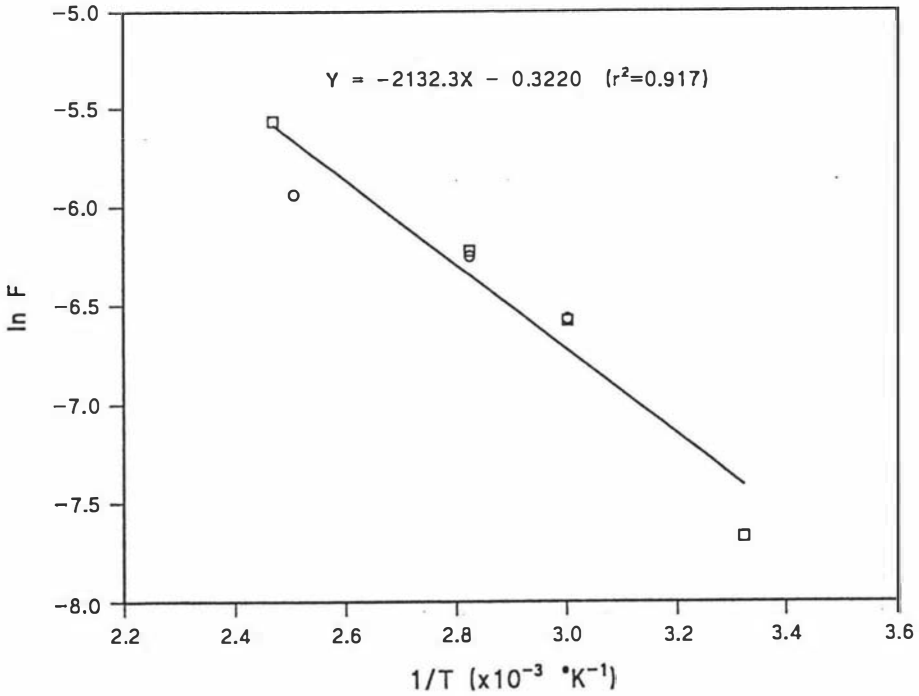


Figure 6.10. Plot of logarithm of FRP drying coefficient against reciprocal of air inlet drying temperature for pilot plant (○) and commercial (□) casein curds dried in a fluidized bed drier at an air velocity of 1.6 m/s and at ambient humidity.

Table 6.6. 'Apparent activation energies' of different biological materials calculated from the FRP drying coefficient.

Product	Temperature Range (°C)	Activation Energy (kJ/mole)
Casein[a]	28 - 132	17.73
French-fry cut Potato[b]	43 - 93	20.02
Steamed Rice[c]	30 - 70	21.71 - 25.72
Unsteamed Rice[c]	30 - 65	31.74
Melon Seed[d]	40 - 60	24.77
Yellow Corn[e]	38 - 104	33.91
Popcorn[f]	38 - 82	35.57

a from this study

b Chiang & Petersen (1985)

c Verma *et al.* (1985)

d Ajibola (1989)

e Ross & White (1972)

f White *et al.* (1981)

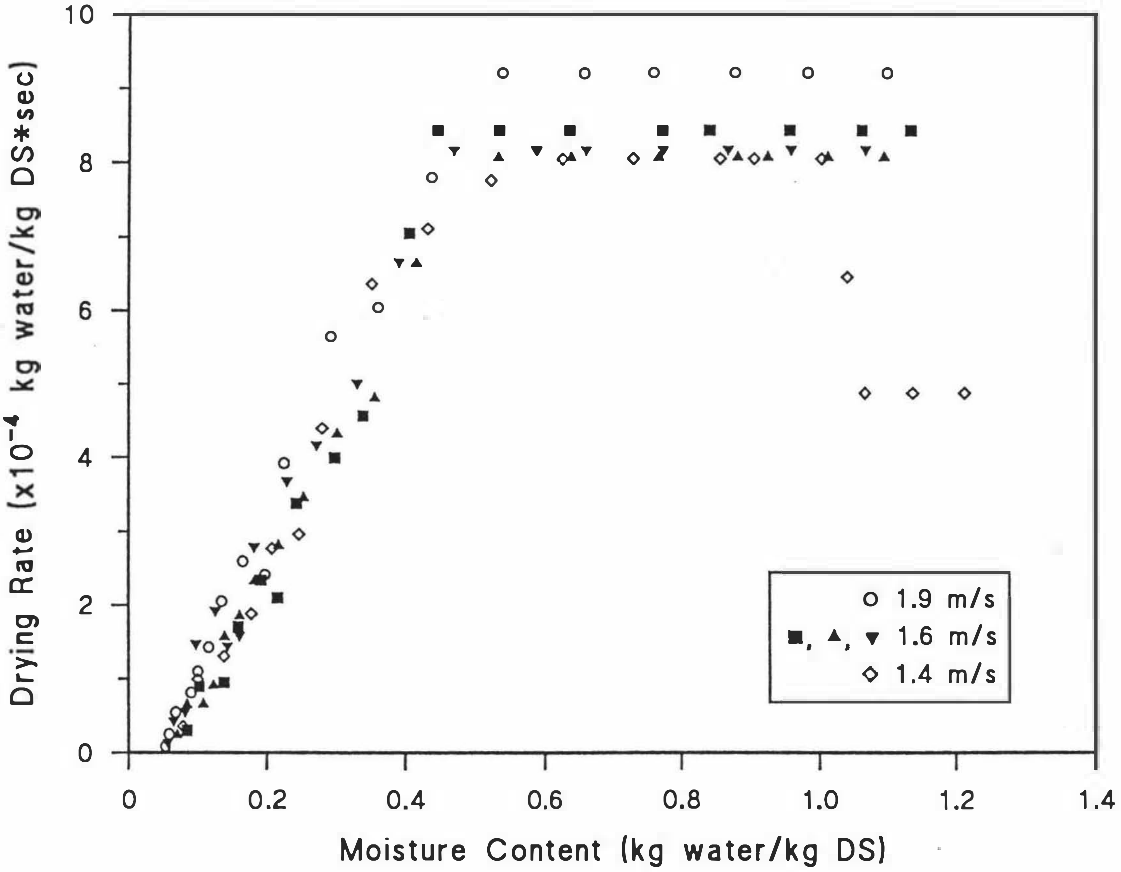


Figure 6.11. Drying rate curves of pilot plant casein curd dried in a fluidized bed drier with different air velocities, an air inlet drying temperature of 81°C and at ambient humidity.

Similar observations were made by Bimbenet *et al.* (1985) for drying of carrot cubes. Although carrot had no constant rate period, the initial part of the drying rate curves increased with air velocity while the later part of the curves were very similar. These results were expected since from drying theory (Nonhebel & Moss, 1971; Williams-Gardner, 1971; Heldman, 1975; Brennan *et al.*, 1976; Watson & Harper, 1988), the main resistance to heat/mass transfer in the CRP is in the gas phase and is reduced when air velocity is increased. In the falling rate period, most of the resistance is in the solid phase and therefore an increase in air velocity is unlikely to have a significant effect.

Drying Rate Curves of Commercial Casein Curd. The effect of air velocity on the drying rate of commercial casein curd was also studied. Air velocities of 1.3, 1.6 and 1.9 m/s were studied while all other conditions were held constant. The average d_{50} for this batch of casein was 1.49 mm.

The drying rate curves for commercial casein curd with different air velocities are shown in Figure 6.12. The results follow the same trend obtained for the pilot plant casein curd. However there was a considerable increase in the CRP drying rate for the 1.9 m/s data. This was probably due to the smaller particle size of the commercial casein curd which was more fluidized thereby exposing more surface area to the drying air. All the data have excellent agreement in the falling rate period because they were all done on the same day which reduced any external fluctuations such as storage effects.

6.4. EFFECT OF MANUFACTURING CONDITIONS ON DRYING RATES

6.4.1. Particle Size

The effect of particle size on the drying rate of casein curd was studied. Using a commercial lactic casein curd, three lots of samples were sieved into size fractions of 0.50-1.00 mm (mean size=0.75 mm), 1.00-2.00 mm (1.50 mm) and 2.00-3.35 mm (2.68 mm) and dried at 81°C. It was not possible to keep the air velocity constant for all runs at 1.6 m/s. The velocity was too high for the 0.75 mm sample and the bed was lost. It was too low for the 2.68 mm sample as the bed did not fluidize. After preliminary runs, the 0.75 mm sample was dried at an air velocity of 1.3 m/s, the 2.68 mm sample at 1.9 m/s and the 1.50 mm sample at 1.6 m/s.

Figure 6.13 shows the drying rate curves for commercial casein curd for different particle size fractions and air velocities. Air velocity did not affect the drying rates in

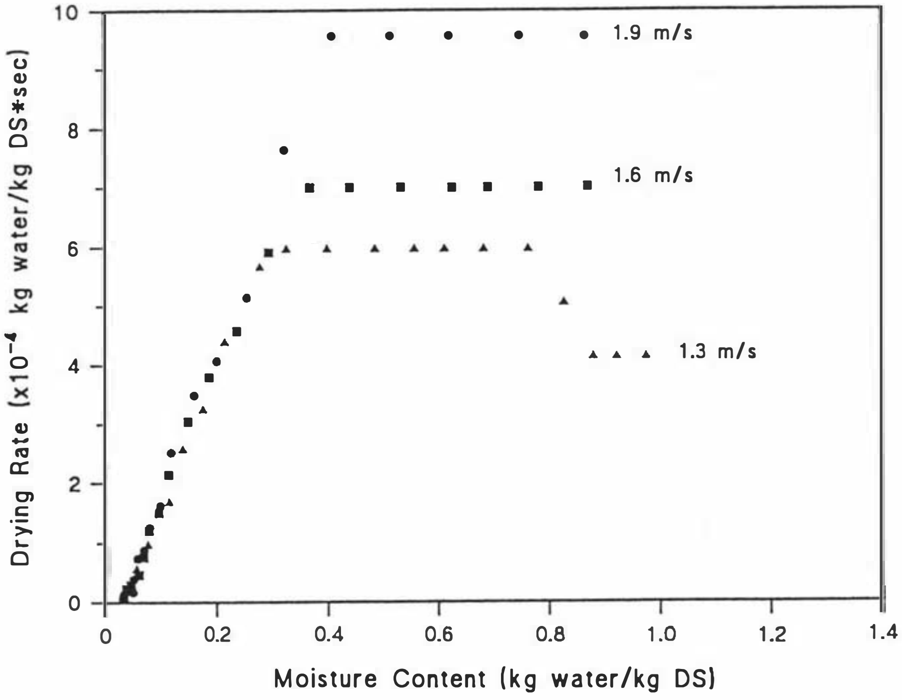


Figure 6.12. Drying rate curves of commercial casein curd dried in a fluidized bed drier with different air velocities, an air inlet drying temperature of 81°C and at ambient humidity.

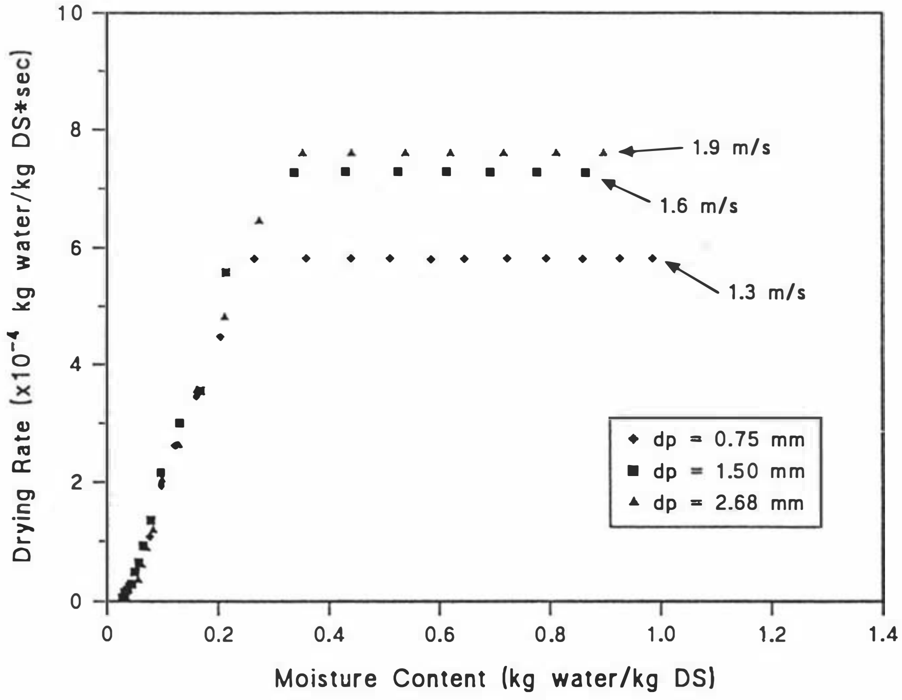


Figure 6.13. Drying rate curves of commercial casein curd with different mean particle sizes (dp) and dried in a fluidized bed drier with different air velocities, an air inlet drying temperature of 81°C and at ambient humidity.

the falling rate period as shown in Section 6.3.2, and particle size did not seem to be a factor either.

The effect of particle size and air velocity on the constant rate period is difficult to determine without closer analysis. Plots of CRP drying rates against air velocity for commercial casein curd samples with relatively uniform size and mixed size (from Figure 6.12) are shown in Figure 6.14. The plot suggest that the CRP drying rate is related to particle size in a non-linear manner. At an air velocity of 1.3 m/s, there was not much difference in the drying rates between the mixed sample and the 0.75 mm sample. This is probably because the drying rate considered for the mixed sample was after the unsteady period, hence the particles had partly dried and the particle density changed which may have produced the same flow pattern as for the 0.75 mm sample. The CRP drying rate for the 1.50 mm sample was very similar to that for the mixed sample at an air velocity of 1.6 m/s. At the highest velocity of 1.9 m/s, the mixed sample and the 2.68 mm samples have completely different flow patterns. The 2.68 mm sample had a lower overall surface area for drying than the mixed sample which resulted in a lower drying rate at the same air flow. The bigger sample also did not fluidized as easily, resulting in poorer air mixing with casein and more bypassing.

6.4.2. Precipitation pH

The effect of precipitation pH on the drying rate of pilot plant casein curd was studied. The Alfa Laval decanter was used for dewatering the casein curd. Samples of casein curd precipitated at a pH of 4.3, 4.6 and 4.8 were dewatered at 30^{O}C. The samples were dried in the fluidized bed drier at the standard drying conditions.

Figure 6.15 shows the drying rates curves for pilot plant casein curd manufactured at different precipitation pH's but dewatered at the same temperature. An increase in precipitation pH caused a considerable reduction in the CRP drying rate but the drying rates in the FRP seemed to be affected only slightly. Table 6.7 shows the results of the analyses of the drying data.

Casein curd precipitated at low pH results in a greater curd volume (O'Meara & Munro, 1982), lower solids content (Jablonka & Munro, 1986a), smaller particle size (Jablonka & Munro, 1985) and weaker curd (Jablonka & Munro, 1986b). Hence the low pH sample has a more open structure and smaller particle size which resulted in a greater surface area and possibly better air/casein mixing thereby increasing the drying rate in the constant rate period. However this loose structure clearly seals up sooner (as observed visually) giving a higher critical moisture content than the other two samples.

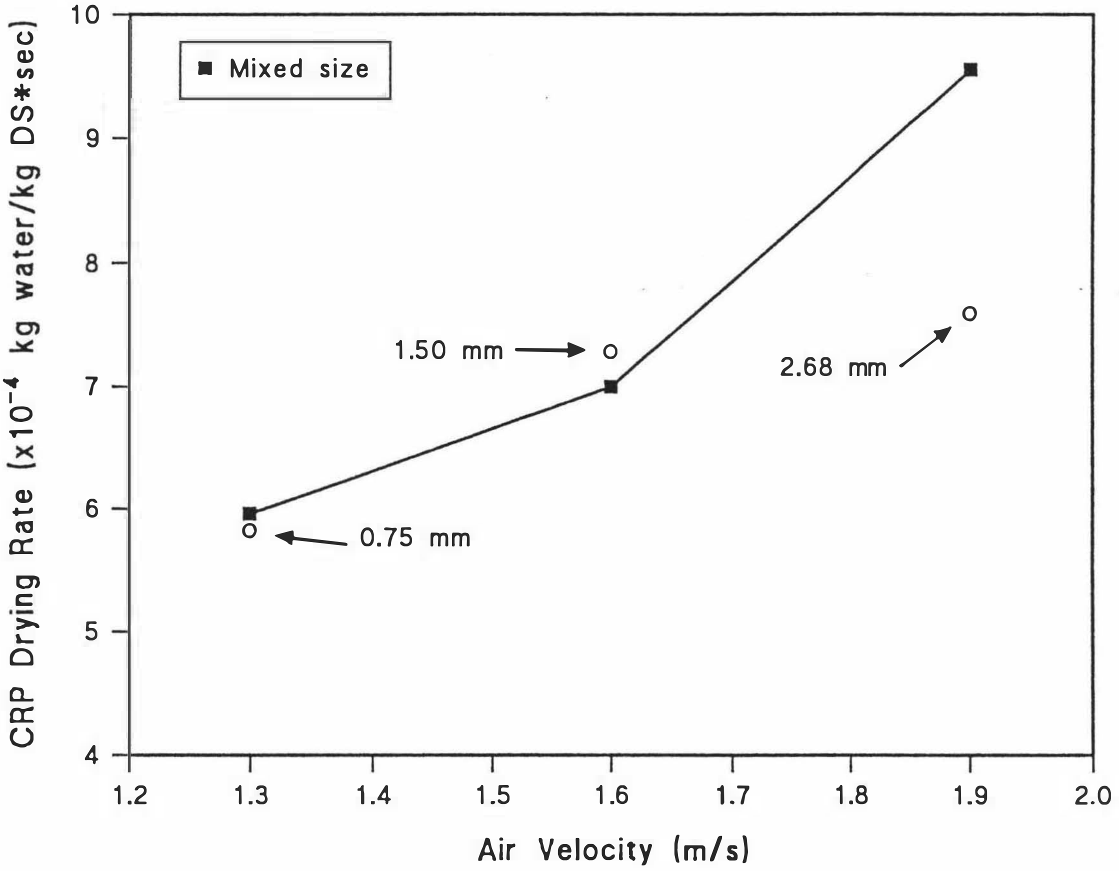


Figure 6.14. A plot of CRP drying rate against air velocity of commercial casein curd with mixed and uniform sizes dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

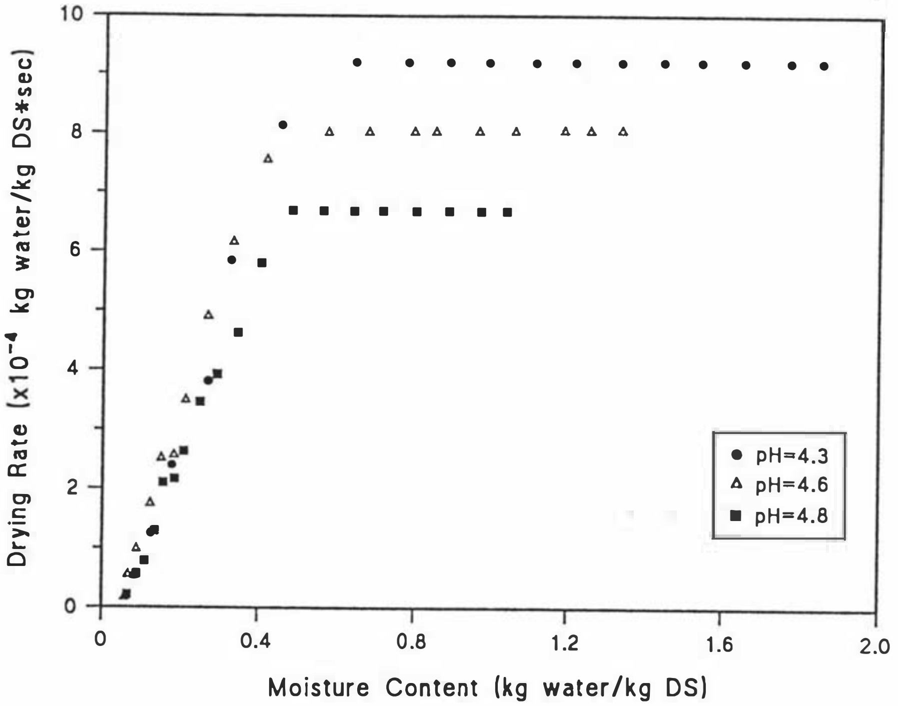


Figure 6.15. Drying rate curves of pilot plant casein curd with different precipitation pH and dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Table 6.7. Drying data for pilot plant mineral acid casein curd with different precipitation pH and dewatered at 30°C (Alfa Laval Decanter) dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Precipitation pH	Initial MC (kg water/kg DS)	MC at t=0 (kg water/kg DS)	CRP Drying Rate (kg water/ kg DS*sec)	FRP Drying Coefficient (sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC (kg water/kg DS)
4.3	2.126	1.847	0.000921	0.002033	0.069	0.52
4.6	1.443	1.392	0.000792	0.001983	0.039	0.43
4.8	1.178	0.971	0.000642	0.001700	0.072	0.45

The lower FRP drying rate of the high pH sample was probably a result of its compact structure and bigger particle size which hindered moisture diffusion.

The results also show that the initial moisture content of casein curd decreased with an increase in precipitation pH. These results correlated well with those observed by O'Meara and Munro (1982) on the decrease of curd volume with an increase in precipitation pH and Jablonka and Munro (1986a) on the increase in solids content with an increase in precipitation pH.

6.4.3. Dewatering Temperature and Degree of Plasticization

Constant Precipitation pH. The effect of the degree of plasticization on the drying rate of pilot plant casein curd was studied. Using the Alfa Laval decanter, different dewatering temperatures were used to achieve different degrees of plasticization. The dewatering temperatures used were: 32^{o}C (standard); 42^{o}C (semi-plasticized); and 52^{o}C (plasticized). The casein curd samples were dried at the standard drying conditions.

The drying rate curves for pilot plant casein curd with different dewatering temperatures are shown in Figure 6.16. Table 6.8 summarizes the results of the analyses of the drying data. The semi-plasticized casein curd dries to the same apparent EMC as the standard sample but at a much higher rate in the falling rate period. The plasticized curd shows the same rate of drying as the semi-plasticized sample, but cannot be dried to the same low EMC, i.e. some moisture is 'locked in' to the plasticized curd in some way. The two plasticized samples had lower critical moisture contents than the standard sample, suggesting a rigid structure delaying the surface sealing effect.

The standard and the semi-plasticized samples have similar CRP drying rates but the plasticized sample has a significantly lower CRP drying rate. This is probably because of reduced porosity and reduced surface area for the plasticized sample. Espie *et al.* (1984) also reported lower CRP drying rates, lower critical moisture contents and higher final moisture contents (approximating the EMC) for plasticized casein as compared to a standard mineral acid casein.

Different Precipitation pH. In the commercial plants, the operators usually increase the dewatering temperature of curd with low pH to agglomerate the particles and reduce the fines carry-over or decrease the dewatering temperature of high pH curd to prevent plasticization which can further increase the particle size. This study

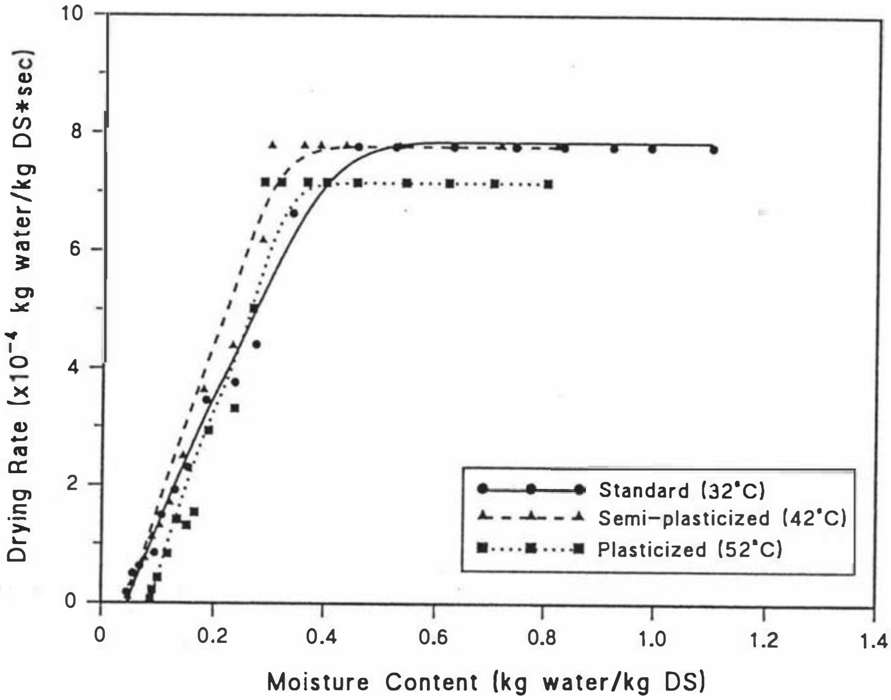


Figure 6.16. Drying rate curves of pilot plant casein curd dewatered in an Alfa Laval decanter at different temperatures and dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity (temperatures in parentheses refer to the dewatering temperature).

Table 6.8. Drying data for pilot plant mineral acid casein curd with different dewatering temperatures (Alfa Laval Decanter) dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Dewatering Temp. (°C)	Initial MC (kg water/kg DS)	MC at t=0 (kg water/kg DS)	CRP Drying Rate (kg water/ kg DS*sec)	FRP Drying Coefficient (sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC (kg water/kg DS)
32	1.312	1.102	0.000783	0.001939	0.035	0.43
42	0.970	0.819	0.000778	0.002453	0.043	0.36
52	1.002	0.802	0.000681	0.002365	0.081	0.37

determined the effect of this practice on the drying rates of the resulting casein curd.

Casein curd samples from the same batch were used to study the effect of precipitation pH at the same dewatering temperature (Section 6.4.2.). The low pH sample (pH=4.3) was also dewatered at 45°C to further agglomerate it as the resulting curd at 30°C was fine and soft. The high pH sample (pH=4.8) was also dewatered cold at 24°C to prevent plasticization which can increase the particle size.

Figure 6.17 shows the effect of precipitation pH and dewatering temperature on the CRP drying rates including data from Figure 6.16. The drying rate in the constant rate period decreased with an increase in dewatering temperature at all pH's examined. At the same dewatering temperature, the CRP drying rate increased with a decrease in pH. The results also suggest that for curd at the optimum pH of 4.6, the dewatering temperature does not have a major effect on CRP drying rate.

The effect of precipitation pH and dewatering temperature on the FRP drying coefficient is presented in Figure 6.18. The FRP drying coefficients of the two lower pH samples increased with dewatering temperature. But for the high pH sample the opposite effect was observed. At low pH, the sample with the higher dewatering temperature may have sufficient rigidity from the effect of plasticization that it did not shrunk to the same extent, resulting in a higher FRP drying coefficient. The high pH sample dewatered at the higher temperature may have created a more compact and rigid structure which hindered moisture diffusion in the FRP hence decreasing the drying coefficient.

Comparison with the Tunnel Dried Casein Curd. The results obtained from the tunnel drying study were different to those from the fluidized bed drying study. The differences between these two drying methods are summarized in Table 6.9.

The higher drying rates of the samples dried in the fluidized bed drier were due to the higher surface area exposed and better air/particle contact during drying which effectively shortened the moisture diffusion path. The two plasticized samples in the tunnel drier were rewetted to increase their initial moisture content from 1.0 kg water/kg dry solids to 1.4 kg water/kg dry solids. The purpose of this was to ensure that the samples had the same initial moisture content as the standard sample (Section 5.1.3). This artificially added water may have caused the considerable increase in the CRP drying rates of the two plasticized samples, the higher CRP drying rate of the plasticized sample and the higher critical moisture contents of the two plasticized samples. Lastly, fluidized bed drying of casein was much faster than tunnel drying

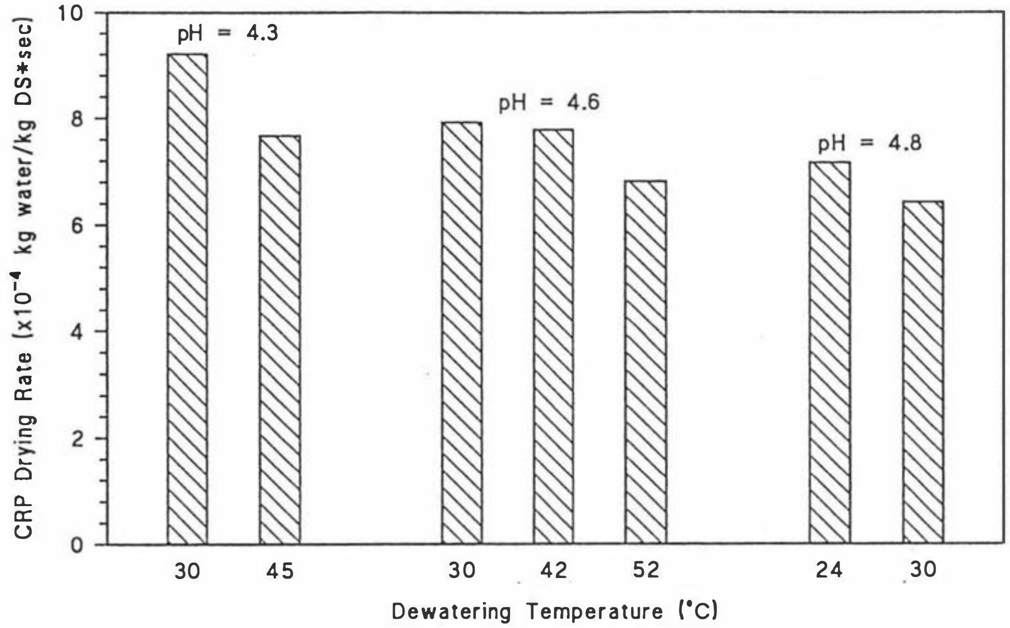


Figure 6.17. The effect of precipitation pH and dewatering temperature on the CRP drying rate of casein curd dried in a fluidized bed drier at an an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

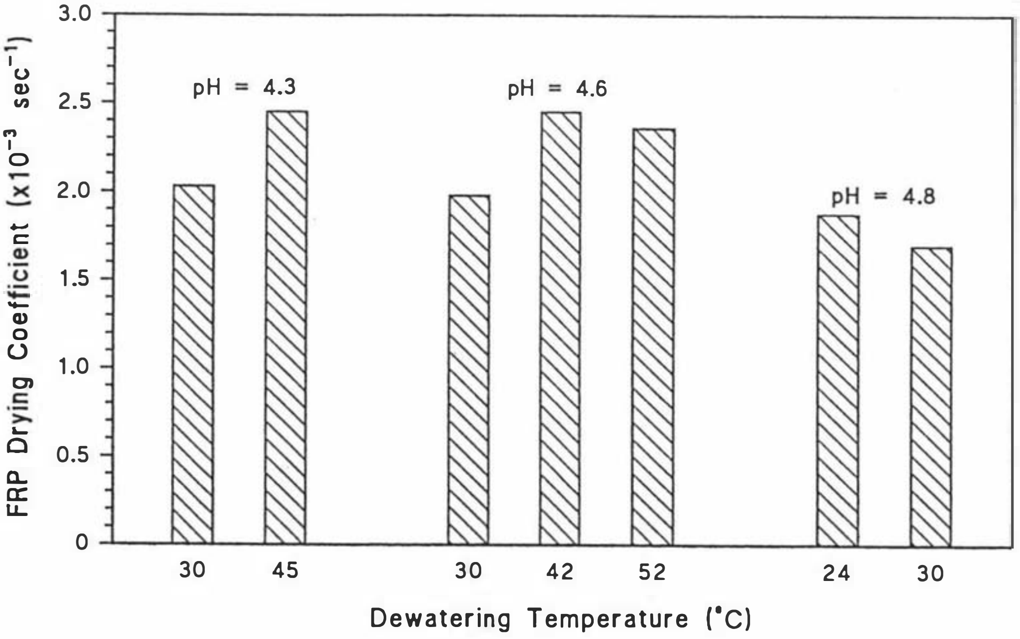


Figure 6.18. The effect of precipitation pH and dewatering temperature on the FRP drying coefficient of casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Table 6.9. Comparison of standard and plasticized casein samples dried in a fluidized bed drier and a tunnel drier.

Fluidized Bed Drier	Tunnel Drier
1. All the casein samples had higher drying rates in the CRP and the FRP.	1. All the casein samples had lower drying rates in both periods as compared with those from the FBD.
2. The standard sample had higher CRP drying rate than the plasticized sample.	2. The standard sample had lower CRP drying rate than the semi-plasticized and plasticized samples.
3. The semi-plasticized sample had higher CRP drying rate than the plasticized sample.	3. The plasticized sample had higher CRP drying rate than the semi-plasticized sample.
4. The two plasticized samples had lower critical moisture content than the standard sample.	4. The two plasticized samples had higher critical moisture content than the standard sample.
5. The semi-plasticized sample had lower apparent EMC than the plasticized sample.	5. The two plasticized samples had similar apparent EMC.

which perhaps ends
the drying much earlier and further away from the real EMC.

6.4.4. Type of Casein Curd

Figure 6.19 shows the drying rate curves for the different types of casein curd from the pilot and commercial plants. Table 6.10 summarizes the drying data using the mathematical modelling procedure. All the types of casein curd were dried at the standard drying conditions. The drying rate in the constant rate period was the highest for rennet casein and the lowest for the commercial lactic casein. However the CRP drying rates of all the pilot plant casein curd samples were similar because they were all within the 95% confidence limits for mineral acid casein (Section 6.2.1). The drying rates in the falling rate period seemed to be affected slightly by the type of casein. The lactic casein from the pilot and commercial plants had the highest FRP drying coefficient followed by rennet casein and mineral acid caseins. Both mineral acid caseins dewatered with different decanters had similar drying rates in the falling rate period. The lactic casein samples from the pilot plant and commercial plant also have similar FRP drying coefficients.

The observed results for the CRP drying rates of the pilot plant samples compare well with those obtained by Espie *et al.* (1984). They found that for the unsized samples, the rennet casein had the highest CRP drying rate followed by the gas-producing lactic casein and then mineral acid casein. The CRP drying rate of the commercial lactic casein was slightly lower than the pilot plant lactic casein. Jablonka and Munro (1987) found that the curd strength for commercial acid caseins were generally higher than for pilot plant caseins. The observed difference is probably related to the interparticle interactions which will be much stronger for commercial casein, perhaps resulting in a lower drying rate.

Espie *et al.* (1984) classified casein according to their ease of drying with rennet casein being the most difficult followed by mineral acid casein and lactic casein being the easiest. This classification was based on the overall drying time for casein and not on rate in any particular drying period. To make a similar comparison the overall drying time of the different types of casein were calculated using the values from Table 6.10. Appendix 6.3 shows a sample calculation for the drying times.

Table 6.11 presents the results of these calculations. The two lactic caseins gave faster overall drying times than the other samples followed by rennet casein and then mineral acid caseins. However, considering the 95% confidence bounds (Appendix 6.4) on the mineral acid casein, the overall drying time of rennet casein was not significantly

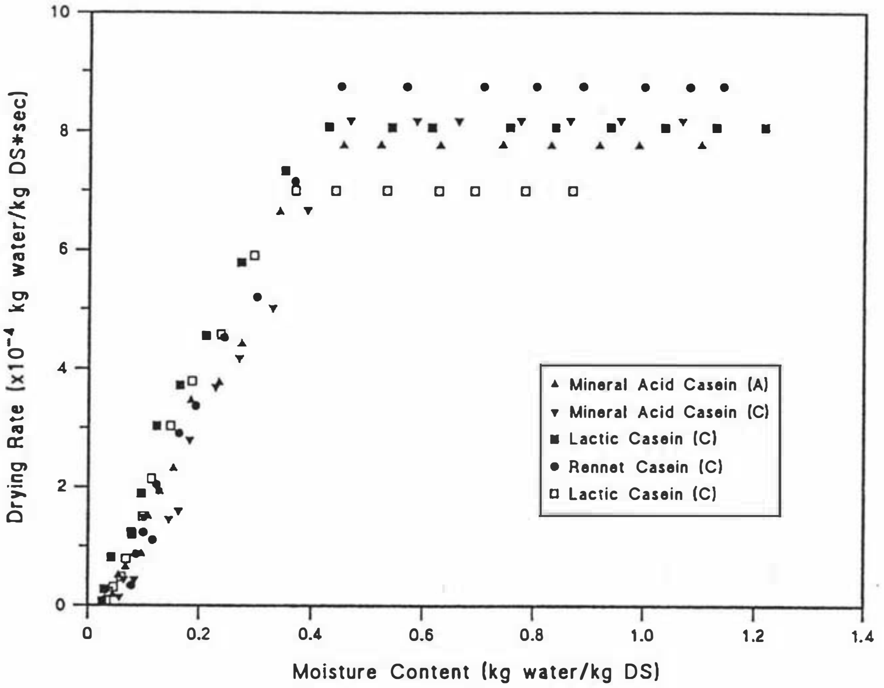


Figure 6.19. Drying rate curves of different types of casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity (solid symbols refer to pilot plant samples and open symbol refer to commercial sample; A – Alfa Laval Decanter and C – Conturbex Centrifuge).

Table 6.10. Drying data for different types of casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Type of Casein Curd	Number of Samples	Average Initial MC (kg/kg)	CRP Drying Rate ($x10^{-4}$ kg water/ kg DS*sec)	FRP Drying Coefficient ($x10^{-3}$ sec^{-1})	Apparent EMC (kg water/kg DS)	Critical MC
Pilot Plant						
Sulph. (C)	10	1.34±0.10	8.02±0.24	1.93±0.05	0.057±0.010	0.47±0.03
Sulph. (A)	4	1.38±0.20	7.84±0.29	1.97±0.07	0.043±0.013	0.43±0.01
Rennet (C)	2	1.45	8.36	2.15	0.044	0.43
Lactic (C)	2	1.20	8.07	2.38	0.024	0.37
Commercial						
Lactic (C)	2	1.15	6.84	2.38	0.036	0.32

where: C - Conturbex dewatered

A - Alfa Laval dewatered

different. In the falling rate period, the lactic casein samples had the shortest drying times followed by rennet casein. Their drying times were significantly shorter than the mineral acid casein samples. The trend of the results obtained were different to those observed by Espie *et al.* (1984). The lactic casein samples dried much faster because of the open and porous structure as compared to the mineral acid and rennet caseins which have more compact structures.

Table 6.11. Drying times for different types of casein curd dried in a fluidized bed drier at an air inlet drying temperature of 81°C, an air velocity of 1.6 m/s and at ambient humidity.

Type of Casein Curd	Time in the Constant Rate Period (minutes)	Time in the Falling Rate Period (minutes)	Overall Drying Time (minutes)
Pilot Plant			
Sulphuric (C)[a]	18.08±2.23	14.28±2.23	32.36±3.15
Sulphuric (A)	20.20	12.06	32.26
Rennet (C)	20.33	11.12	31.45
Lactic (C)	17.14	7.90	25.04
Commercial			
Lactic (C)	20.22	7.31	27.53

a Mean drying time with 95% confidence interval

CHAPTER 7

MEASUREMENTS IN COMMERCIAL CASEIN DRY PROCESSING SYSTEMS

7.1. MEASUREMENTS IN AN NDA VIBRATED BED DRIER

7.1.1. Casein Moisture Changes through the Drier

Measurements in commercial driers were undertaken in the casein plant of Tui Milk Products at Longburn, Palmerston North. The two types of drier which were used in the factory were the Niro fluidized bed drier and the NDA vibrated bed drier.

The first aim of the study was to obtain the drying rates of casein curd in a commercial drier. This was found to be difficult to carry out in the Niro drier because there were insufficient sampling points along the drier. However the NDA drier had at least seven sampling points and this drier was therefore chosen for the study. The NDA drier comprised a 2-deck predrier and a 4-deck final drier.

Figure 7.1 shows the plot of the moisture content of casein against the distance from the predrier inlet for the different sampling points. The approximate temperature of the curd at each sampling point is also shown. It was assumed that the moisture of the curd entering the drier did not fluctuate over the duration of sampling and hence the curd taken at various points was a representative sample. It seemed that the constant rate period for casein drying took place in the predrier. This was supported by the fairly constant temperature of the curd at the first three sampling points. The temperature of casein obtained at the end of the predrier increased which could indicate that the casein may be in the falling rate period. Surprisingly, the curd temperature decreased when it reached the top deck of the final drier. This is probably due to the lower inlet air temperature used in the final drier. The drying of casein in the final drier was entirely in the falling rate period. This conclusion was supported by the increased temperature of casein from the top deck to the end of the final drier.

The moisture content of casein off the NDA predrier was 30.6% (w.b.) and from the NDA final drier was 13.0% (w.b.). Patchett (1968) reported the average moisture contents of casein exiting the Bates predrier as 29.9% (w.b.) and the final drier as 10.1% (w.b.). Since the NDA drier is a modified Bates drier the results are comparable. The moisture content of casein off the predrier compares well with that from the Bates predrier. However the casein moisture content off the final drier was a

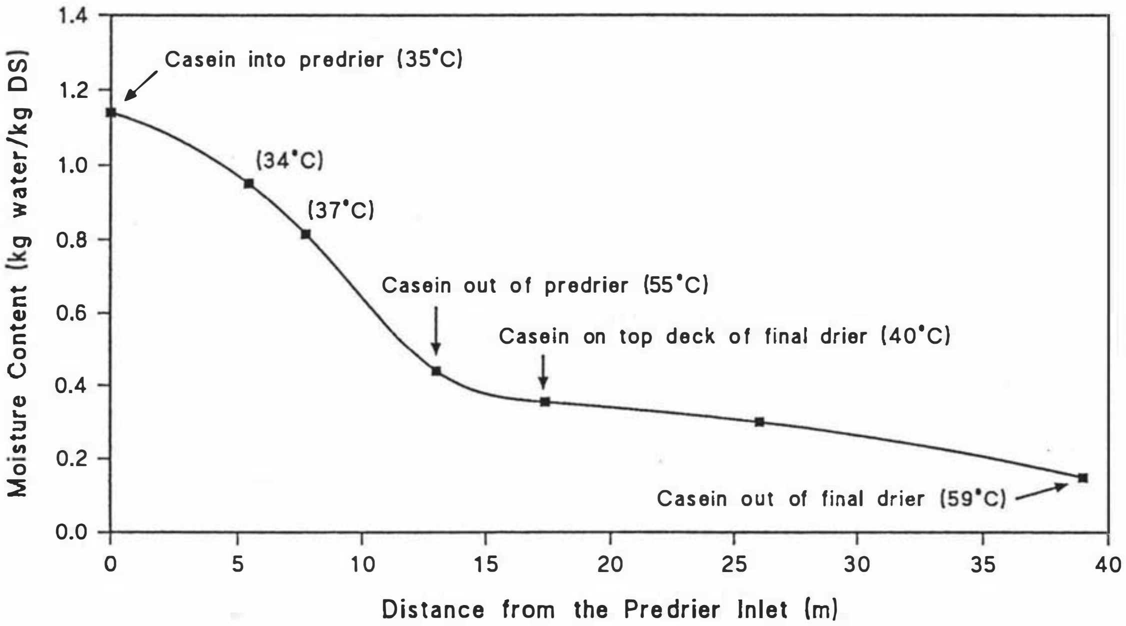


Figure 7.1. Moisture content of casein as a function of distance travelled along the NDA predrier and final drier (temperatures in parentheses refer to the approximate temperature of casein at the sampling point: Predrier inlet temp., 120°C; outlet temp., 40°C and vibrator rpm, 1100: Final drier inlet temp., 100°C; outlet temp., 37°C and vibrator rpm, 770).

little higher than that of the Bates final drier because the target moistures are different. Morison *et al.* (1990) have shown that casein loses some moisture during tempering and blending by conveying with low humidity air (less than 60% relative humidity). For this reason the moisture of the casein leaving the drier is always a little higher than the final target moisture.

7.1.2. Drying and Drying Rate Curves of Casein Curd

Each deck of the predrier and final drier was 6.5 m long. Therefore the total deck length from the inlet of the predrier to the outlet of final drier was 39 m. The overall residence time of casein in the predrier and final drier was determined to be about 8 minutes. This was the elapsed time at start up between entry of the first casein into the predrier and exit of the first casein from the final drier. This residence time determination is very approximate but it is considered probable that the residence time would lie in the range 4 to 16 minutes. For an 8 minute residence time the average speed of casein along the drier would be 5 meters per minute. Therefore Figure 7.1 can be converted to a moisture content versus time curve and treated as similar to a batch drying curve.

A plot of moisture content against time (drying curve) is presented in Figure 7.2 and a fitted drying curve determined as described previously (Chapter 6) even with limited data. The results indicate that the mathematical model described the experimental drying curve satisfactorily. Because there were very few data points, the experimental drying rate curve was obtained from the fitted mathematical model.

Figure 7.3 shows the drying rate curves for casein dried in a commercial NDA drier and a laboratory fluidized bed drier (from Section 6.3.1). The CRP drying rate for casein in the predrier was about three times that obtained from the laboratory fluidized bed drier. This is not surprising because the casein bed depth in the NDA drier is very shallow and is well vibrated. This means there is much better particle/air contact and the drying air is also far less likely to become saturated as it does in the deeper bed in the laboratory drier. The falling rate period occurred in the final drier and the drying rates seemed to be a little higher than those obtained in the laboratory drier. However the magnitude of the drying rates for the two driers are not significantly different considering that the drying rate curve for the commercial drier was derived from the fitted drying curve on limited data points. The casein in the NDA drier seems to have a much higher critical moisture content than that in the laboratory fluidized bed drier. The commercially dried casein is in a shallow bed which resulted in very fast drying. The very fast drying may have resulted in some case hardening which would cause a

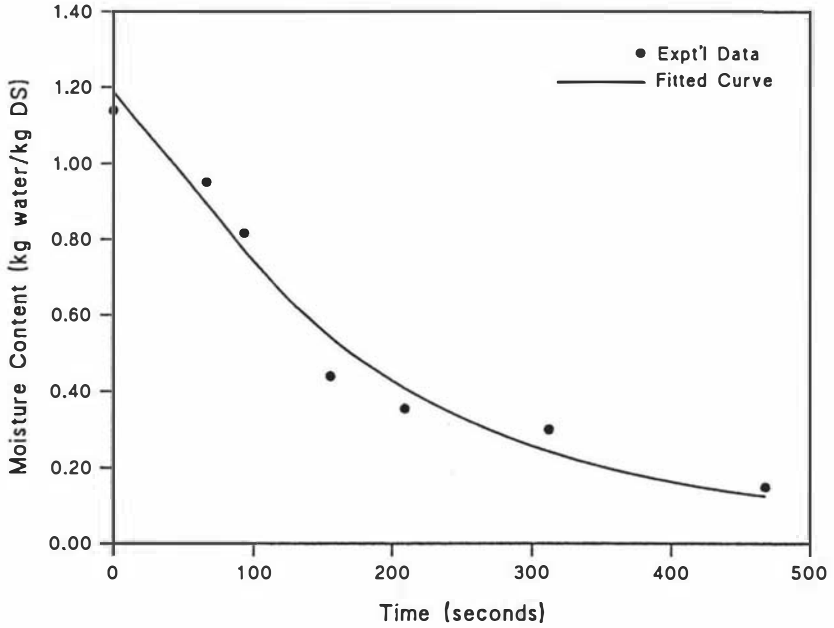


Figure 7.2. A plot of moisture content against time for casein curd dried in an NDA vibrated bed drier (Predrier inlet temp. = 120°C, outlet temp. = 40°C and vibrator rpm = 1100; Final Drier inlet temp. = 100°C, outlet temp. = 37°C and vibrator rpm = 770). Note – The time axis was based on a very approximate residence time of 8 minutes.

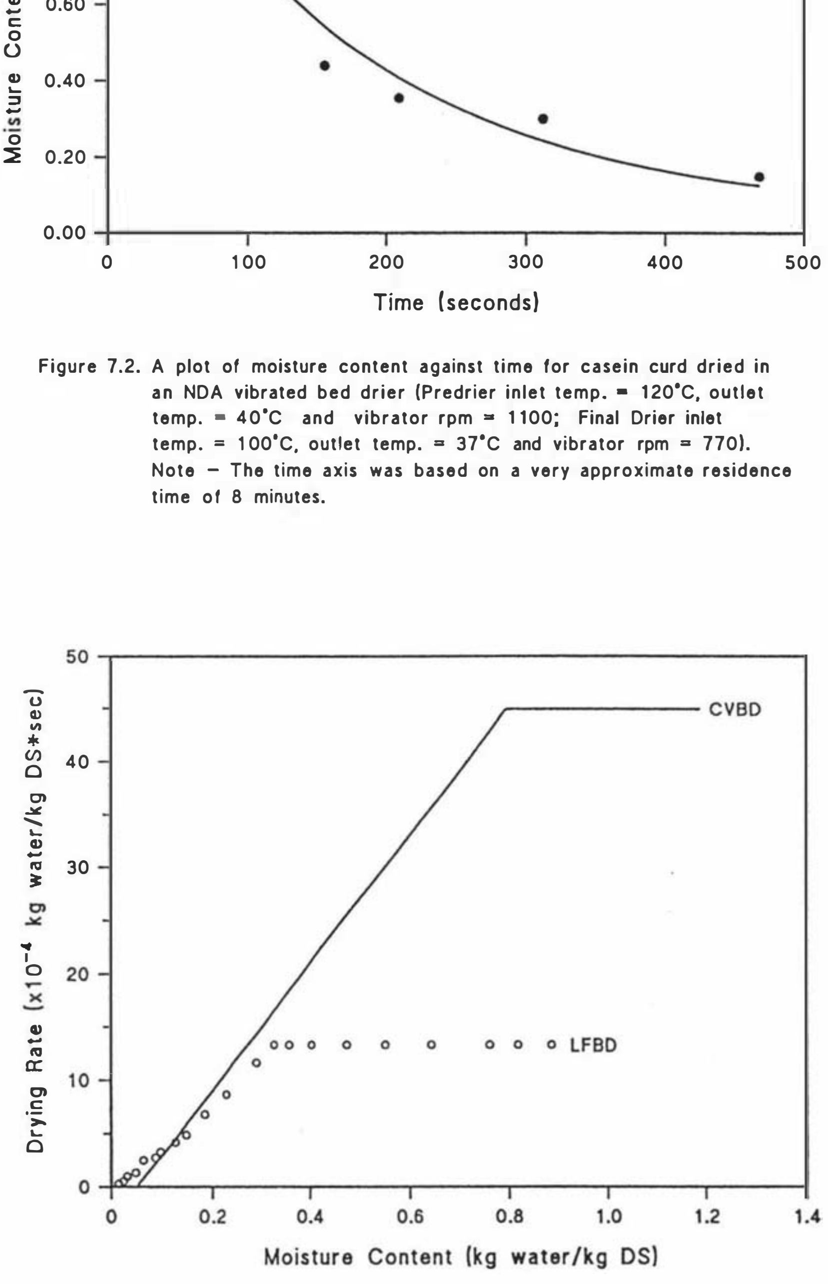


Figure 7.3. Drying rate curves of casein curd dried in the laboratory fluidized bed drier (LFBD) at an inlet temp. of 132°C and the commercial vibrated bed drier (CVBD) with predrier inlet temp. of 120°C and final drier inlet temp. of 100°C. Note – Rate data for CVBD is based on a very approximate residence time of 8 minutes.

higher critical moisture content. In the falling rate period, the moisture loss is no longer dependent on the gas phase heat and mass transfer resistance but is more dependent on diffusion within the casein particle

7.2. MOISTURE CONTENT AS A FUNCTION OF PARTICLE SIZE

7.2.1. Dry Processing System Measurements

The dry processing system referred to covers the casein curd entering the drier to the casein leaving the tempering bin. Tempering is a process carried out immediately after the casein leaves the drier to allow equilibration of moisture both within and between different sized particles (King, 1970; Southward & Walker, 1980). A study was carried out to determine how the moisture content of the different sized particles varied through the dry processing system.

Figure 7.4 shows the moisture content for casein of different size fractions leaving the decanter, the NDA predrier and NDA final drier. The bulk sample referred to is the casein sample from the same batch which has not been sieved. As expected the casein moisture content and particle size decreased as the casein passed through the system. For the casein leaving the decanter, the smaller size fractions were wetter than the other fractions. But at the exit of the NDA predrier and final drier the large casein particles are significantly wetter than smaller casein particles.

During the drying process, the smaller particles dry faster because of a shorter moisture diffusion path and a higher surface/volume ratio. However all the particles shrink as drying proceeds. Using the mean diameter (d_{50}) of the bulk sample to calculate the particle volumes, the percent shrinkage of a particle being dried in the NDA final drier was 51% of the original volume. In comparison, drying a single particle of pilot plant lactic casein in a tunnel drier at a drying temperature of $90^{o}C$ caused a 60% shrinkage (Section 8.3.1).

The moisture content of casein sieve fractions leaving the Niro fluidized bed drier, cooler and tempering bin are shown in Figure 7.5. The data for the moisture content of casein sieve fractions leaving the NDA final drier is also shown for comparison. There was little difference between the moisture content of the casein sieve fractions from the NDA final drier, Niro drier and cooler. They all show that the larger particles were much wetter than the smaller particles. However by the time the casein leaves the tempering bin these variations have been significantly reduced and there is little difference in moisture content between the various size fractions. Because the total

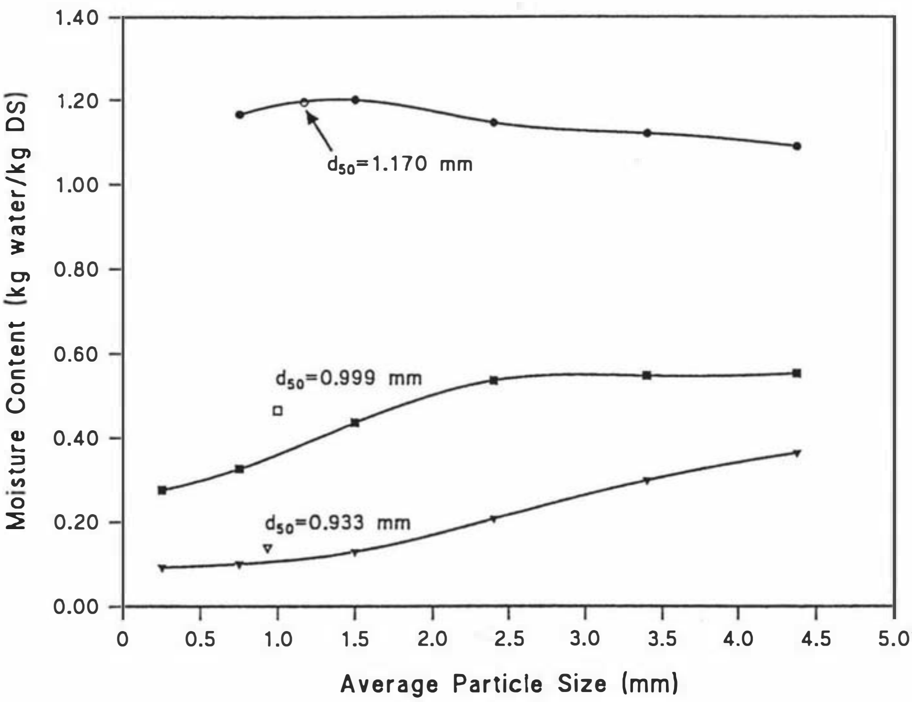


Figure 7.4. Moisture content of casein sieve fractions leaving the decanter (●, ○), NDA predrier (■, □) and NDA final drier (▾, ▿) (open symbols refer to the moisture contents of the bulk samples at their mean diameters, d_{50}).

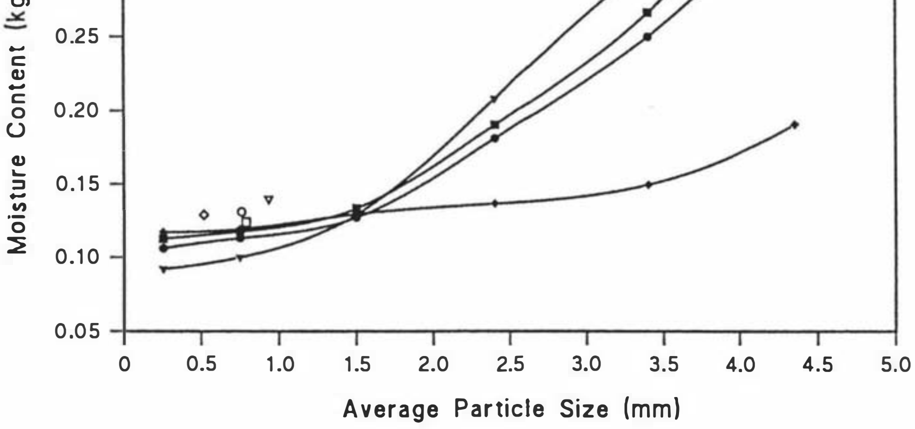


Figure 7.5. Moisture content of casein sieve fractions leaving the NDA final drier (▾, ▿), Niro drier (●, ○), cooler (■, □) and tempering bin (♦, ◇) (open symbols refer to the moisture contents of the bulk samples at their mean diameter, d_{50}).

mass of small particles is so much greater than the larger particles a large drop in moisture content for the larger size fractions has resulted in only a small rise in the moisture content of the smaller size fractions. The moisture content of casein particles increases with particle size for all the samples. Based on the mean particle size, the casein from the NDA final drier was bigger than that from the Niro drier. The casein in the cooler was a mixture of the samples from the NDA and Niro driers. Hence the casein mean particle size was intermediate between the two driers.

7.3.2. Rate of Moisture Equilibration

Neff (1966a & 1966b) stressed the necessity for adequate tempering to provide for efficient cooling and blending of the casein. This step is important to achieve a uniform moisture content for efficient grinding (Muller, 1971) and usually takes about 24 hours (Fox, 1970; King, 1970). The tempering system was studied by determining the rate of moisture equilibration for casein of different size fractions.

The moisture content of casein sieve fractions from the NDA final drier that were stored in a closed plastic bag for various times are shown in Figure 7.6. Initially the bigger particles had a much higher moisture content than the smaller particles. However over a period of time the moisture of the bigger particles diffused out to the smaller particles as shown by the decrease in the moisture of the bigger particles and the subsequent increase in moisture of the smaller ones. This moisture equilibration is almost complete after the third hour since there is little further change between 3 and 24 hours. For this factory at this time clearly a much shorter tempering time than 24 hours would achieve moisture equilibration. It is possible that some other change in the casein mechanical properties also occurs during tempering.

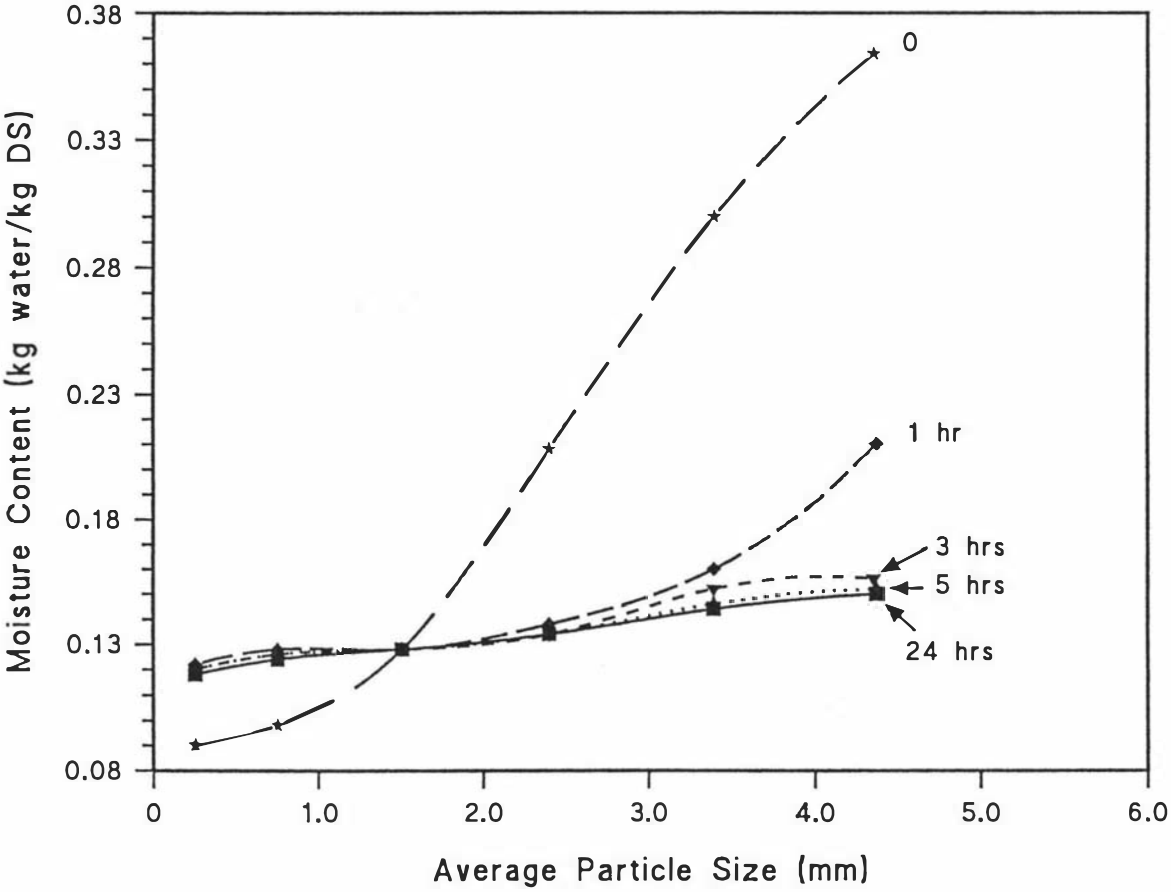


Figure 7.6. Moisture content as a function of particle size for casein from the NDA final drier in a closed plastic bag for various times.

CHAPTER 8
PHYSICAL CHANGES ON DRYING A SINGLE CASEIN PARTICLE

8.1. PRELIMINARY MEASUREMENTS OF CASEIN PARTICLE VOLUME

In order to determine the physical changes on casein particles, it was necessary to determine the volume of the particle accurately. The first attempt to determine the casein particle volume was to assume it to be spherical in shape. The casein particle diameter was measured three times at three points using a vernier caliper. The mean diameter was used in calculating the average volume of the casein particle. After several experiments this procedure was discontinued because of inconsistent results. The inconsistencies from this procedure arose from the irregular shape of casein particles. Most of the casein particles were not spherical in shape at all. In addition, it was difficult to locate the exact measuring points on the casein particle before and after drying in order to follow the extent of shrinkage.

8.2. SEED VOLUME DISPLACEMENT

Because of the inconsistencies in measuring the particle diameter a seed volume displacement method was developed. The method was tested on spherical objects of known diameters. Figure 8.1 indicates that the volume determined by seed displacement slightly overestimated the actual volume of the object. The regression equation is,

$$\text{Seed Volume Displaced} = 1.0535 \text{ Actual Volume} + 0.0433 \quad (\text{cm}^3) \qquad (8.1)$$

Equation 8.1 was applicable for particles with volumes between 0.45 cm^3 and 3.88 cm^3. The coefficient of determination of the equation was 1.000.

The overestimation of the actual volume using this procedure was probably due to the small volume of the objects in relation to the size of the seeds used. However, the *Maku lotus* seeds were the smallest seeds found suitable for this purpose. If the objects to be measured were very much bigger than the seed diameter, i.e. a bread loaf whose volume is usually more than 100 cm^3 (MacRitchie, 1981) the overestimation of the actual volume would become negligible.

8.3. PHYSICAL CHANGES OF CASEIN PARTICLES DURING DRYING

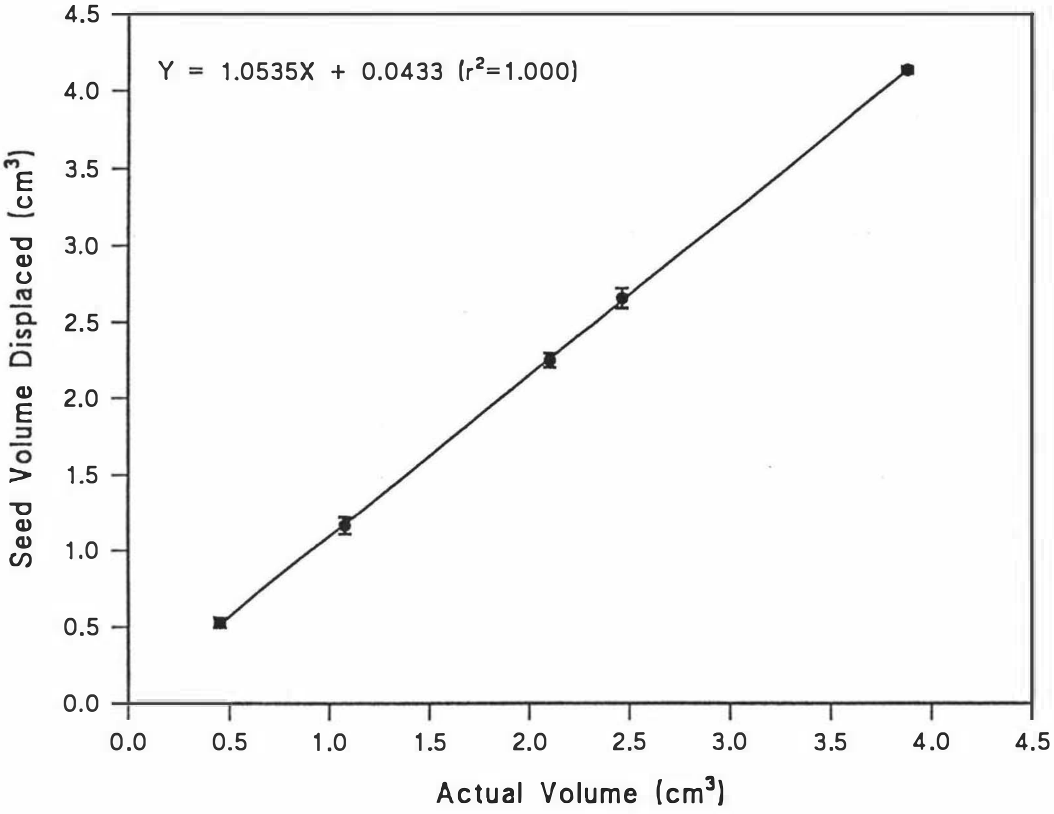


Figure 8.1. A plot of the actual volume of spherical particles against the volume displaced using the seed volume displacement procedure.

8.3.1. Wet and Dry Casein Particles

Casein curd particles shrink during drying. Experiments were carried out to determine how the proportions of air, water and casein in a curd particle changed during drying for the different types of casein.

Table 8.1 presents the results of these investigations on laboratory mineral acid, pilot plant mineral acid, rennet and lactic and commercial lactic caseins. The laboratory made mineral acid casein had the highest initial moisture content because it was dewatered by hand pressing only while the other caseins were mechanically dewatered. The proportion of casein present in the wet curd was lowest in both lactic casein samples (pilot and commercial plants). Similar results were noted by Jablonka and Munro (1987) in comparing the solids content of the different types of commercial casein curd after the last wash. The lactic casein samples had the highest air content which is a result of the porous nature of the curd due to the gas generated by the lactic starter bacteria (Hobman & Hughes, 1977). The amount of casein present in the wet curd for the rennet and the two mineral acid caseins were similar, but rennet casein had more water and less air than the pilot plant mineral acid casein and lactic casein. Espie *et al.* (1984) also reported that the pilot scale rennet casein had the highest initial moisture as compared to the other types of pilot scale casein.

The dried laboratory mineral acid casein had more casein content and less air content than the pilot plant mineral acid casein. It is possible that these differences were due to the difference in manufacturing methods. Firstly, the laboratory casein was precipitated from reconstituted skim milk while the pilot plant casein used fresh skim milk. Secondly, the laboratory casein was precipitated using the heat/acid method batchwise as compared to the pilot plant casein which utilised the acid/heat method in a continuous process. The laboratory casein was washed in water batchwise while a continuous process was used for pilot plant casein. Finally, the pilot plant casein was dewatered more thoroughly than the laboratory casein so that more air was drawn into the dewatered particles as they expanded after dewatering. Hence, all of these factors may have contributed to the differences observed for the two samples. The dried pilot plant mineral acid and rennet casein samples had very similar composition and both samples differed only slightly from the pilot plant lactic casein composition. The two dried lactic caseins had similar volume composition since both employed very similar manufacturing procedures. As expected both lactic casein samples had a lower casein content and a higher air content because of the open and porous structure (Hobman & Hughes, 1977).

Table 8.1. Percentage volume of casein, water and air components and the percent shrinkage of particle for casein curd dried in a tunnel drier at an inlet DBT of 90°C, air velocity of 5 m/s and ambient humidity. Values quoted are mean with 95% confidence limits.

	LABORATORY	PILOT PLANT			COMMERCIAL
	Mineral Acid	Mineral Acid	Rennet	Lactic	Lactic[a]
Init. MC (% db)[b]	165±11	104±6	130±12	115±3	86±12[c]
Final MC (% db)	8.0±4.5	1.8±0.2	2.5±1.8	1.9±0.1	0.4±0.2
Drying Time (hrs)	5.58	5.00	4.65	4.55	2.50
WET CASEIN					
% Casein	26±1	24±1	24±2	18±1	21±2
% Water	60±2	34±2	46±7	29±1	25±2
% Air	14±3	42±3	30±9	53±2	54±4
DRY CASEIN					
% Casein	49±4	38±1	40±2	33±2	35±4
% Water	5±3	1±0.1	1±1	1±0.1	0.2±0.1
% Air	46±4	61±1	59±3	66±2	64.8±4.0
% Shrinkage[d]	55±5	62±2	60±5	55±2	60±7

a dried in an air oven at 100°C

b % dry basis = kg water/100 kg dry solids

c some moisture loss occurred before the experiment

d defined as (dry particle volume/wet particle volume)x100%

The results also indicated that for all the types of casein the shrinkage was very similar at around 55-62% of the original volume. The shrinkage of casein particles was less than that found for root vegetables (Lozano *et al*., 1983; Suzuki *et al*., 1976) presumably due to the higher initial moisture of the vegetables but also differences in cell structure of the vegetables. The root vegetables had initial moisture contents between 2 to 7 kg water/kg dry solids (Lozano *et al*., 1983; Suzuki *et al*., 1976).

8.3.2. A Drying Casein Particle

A study was conducted to monitor the volume reduction of the particle and the relative composition of its components during drying. Figure 8.2 shows the percentage volume reduction of the whole particle and the different components against moisture content. The percentage volume is expressed as the volume of the particle (or component) divided by the original volume of the particle (or component). It was found that the volume of the particle and the air decreased as the moisture content decreased. The volume of air decreased down to a moisture content of about 0.40 kg water/kg dry solids after which there was a slight increase until around 0.04 kg water/kg dry solids. Below 0.04 kg water/kg dry solids the particle volume and the air content decreased slightly. The calculation method assumed that the volume of casein remained constant throughout.

The results suggest that the particle shrinkage is brought about by the loss of water and air from the particle. The casein solids contract around the space left behind by the evaporating moisture. This contraction clearly also squeezes some air out of the particles. However, after a while (below 0.40 kg water/kg dry solids) the casein solids can no longer contract as easily to fill the space left behind by the evaporating moisture. The space becomes air pores resulting in a slight increase in the air content until 0.04 kg water/kg dry solids. As a result of these changes, the particle volume decreases somewhat more slowly in the moisture content range 0.4-0.04. But below 0.04 kg water/kg dry solids, it seems that the casein contracts again resulting in a sharp reduction in particle volume and calculated air volume. This phenomenon is not understood but may be a conformational change in the casein molecule as the last monolayer of moisture is removed. The conformation change may lead to a change in casein density (rather than a reduction in air volume) or to a tightening of the casein matrix squeezing out air.

These observations are different from those described by Kilpatrick *et al*., (1955) for drying vegetable pieces. The shrinkage in volume of vegetable pieces nearly equals the volume of water lost by evaporation in the early stages of drying but in the later stages,

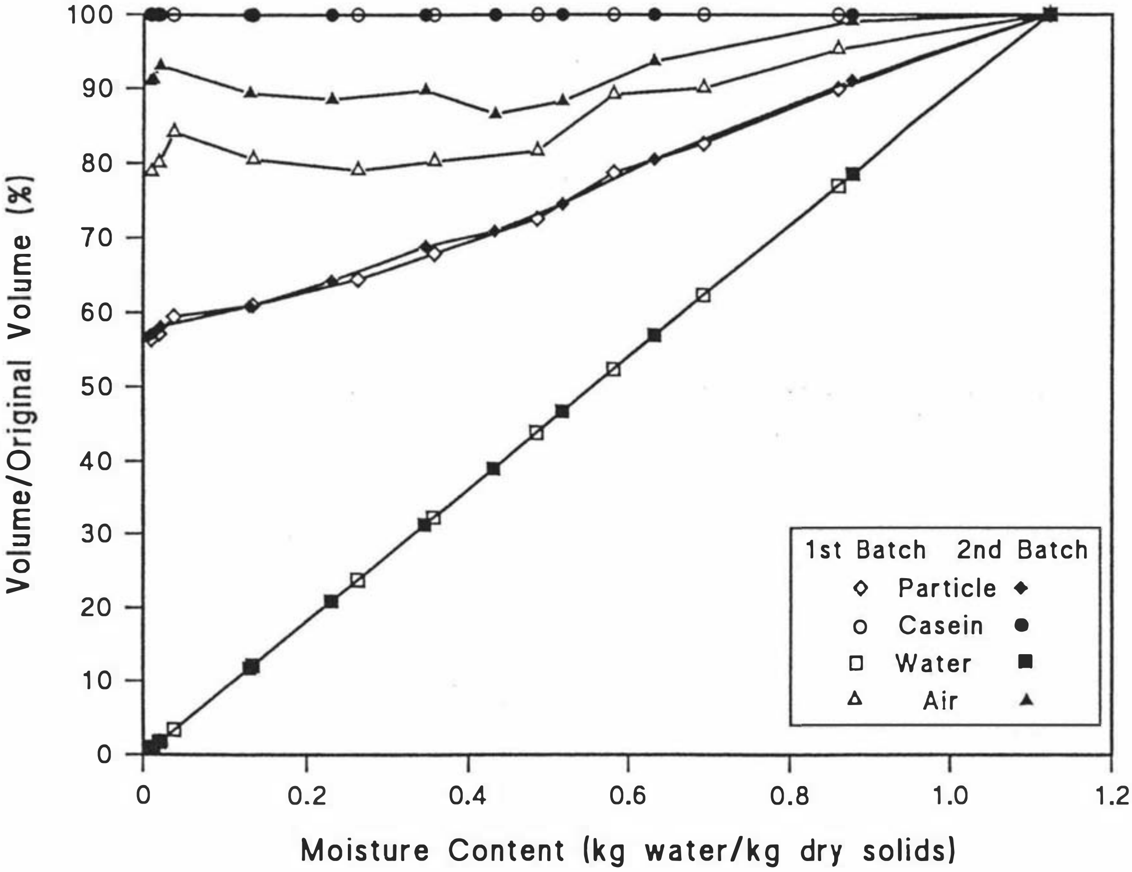


Figure 8.2. Percentage volume reduction of the whole particle and the casein, air and water components during casein drying in a tunnel drier at an inlet DBT of 90°C, air velocity of 5 m/s and at ambient humidity.

shrinkage is greatly reduced. When the moisture content falls below about 20% (w.b.) no further significant shrinkage occurs. This may be due to the cellular nature of vegetables resulting in more rigid structures (Van Arsdel *et al.*, 1973) which are able to resist shrinkage as compared to casein particles which do not have a cellular structure.

Figure 8.3 shows the percentage volume composition of a drying casein particle. The percentage volume is expressed as the volume of the component within the particle divided by the volume of the shrinking particle. The results show that the percentage volumes of casein and air increased while the percentage volume of water decreased as moisture content decreased. In the early stages of drying the proportion of air in the particle increased slowly but it begun to increase more rapidly when the moisture content had fallen to 0.40 kg water/kg dry solids.

Drying a casein particle causes water loss and the loss of this water volume causes a corresponding reduction in the particle volume. However, the particle shrinks even more than can be accounted for by the water loss so that some of the air originally in the particle is squeezed out. This loss of air from the particles occurs mainly at the beginning and end of drying (i.e. moisture content above 0.40 kg water/kg dry solids and moisture content below 0.04 kg water/kg dry solids).

8.3.3. Schematic Representation of a Drying Casein Particle

Using the average data from Figures 8.2 and 8.3, a schematic representation for the physical changes of a drying casein particle was obtained (Figure 8.4). The volume of the casein particle is represented as the area of the circle shown. This observation can be related to the decrease in the radius of the circle containing the casein and air components (R1). The casein content is constant therefore the decrease of this radius is related to the air content. From the 100% down to 63% particle volume the radius decreased which corresponded to the decrease in air content. The radius increased at 58% particle volume showing that the proportion of air increased slightly. Below 0.04 kg water/kg dry solids the air content decreased again as shown by the decrease in the radius. The rate of decrease in the volume of water was constant down to casein bone dry mass.

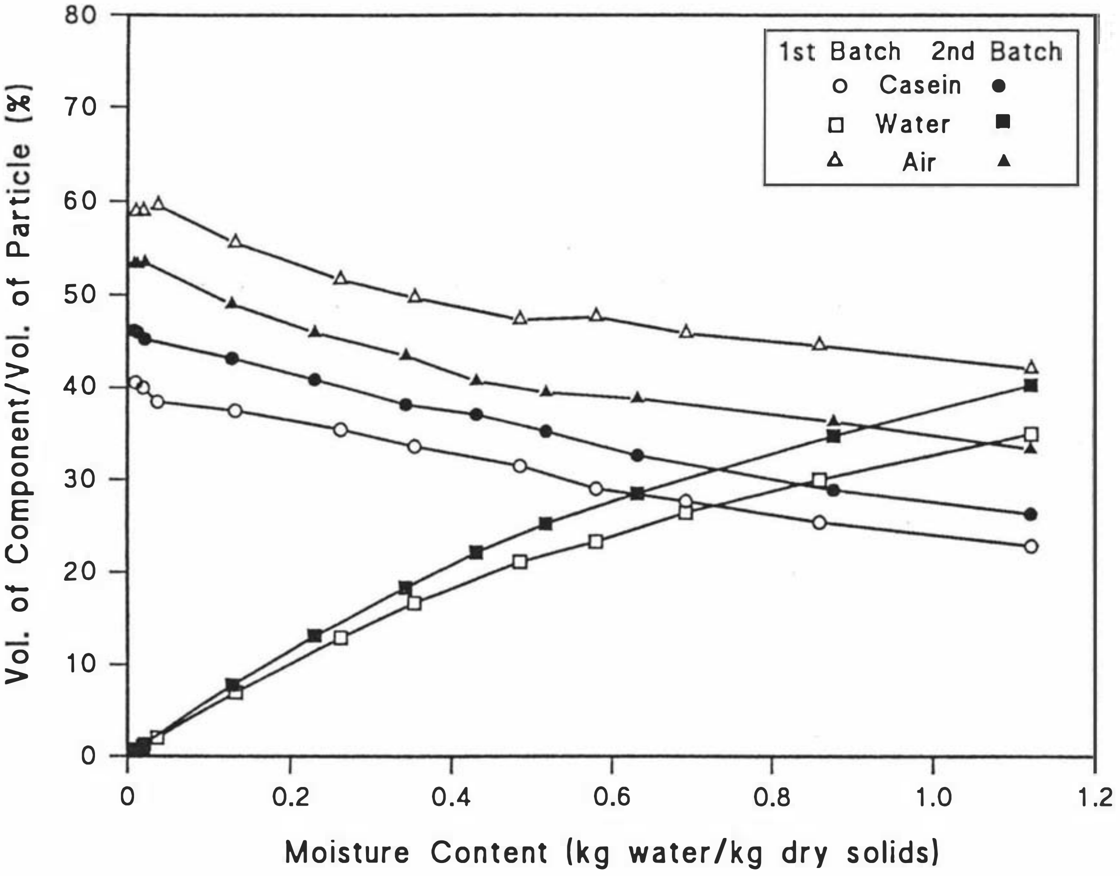


Figure 8.3. Changes in the percentage volume composition of a casein particle as it dries in a tunnel drier at an inlet DBT of 90°C, air velocity of 5 m/s and at ambient humidity.

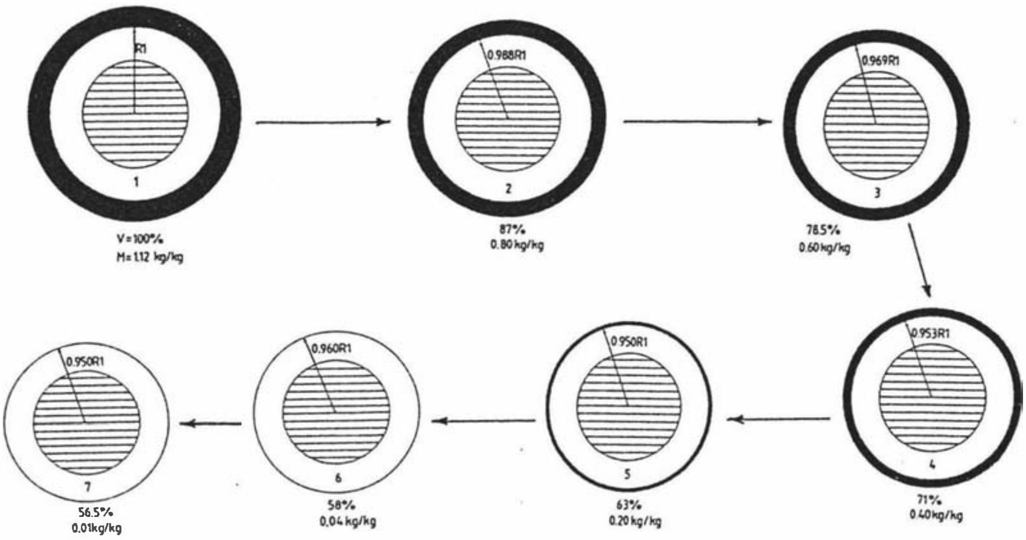


Figure 8.4. Schematic representation for the physical changes during drying a single casein particle (casein ▤, air ☐ and water ■; see Table 8.2 for key to sample conditions). Area on this diagram represents volume of the component.

Table 8.2. Sample conditions for drying a single casein particle (see Figure 8.4).

Sample Code	Moisture Content (kg water /kg DS)	% Particle	% Casein	% Air	% Water	Relative Radius[a]
1	1.12	100.0	24.5	38.0	37.5	R1
2	0.80	87.0	28.2	42.0	29.8	0.988R1
3	0.60	78.5	31.2	43.6	25.2	0.969R1
4	0.40	71.0	34.5	45.5	20.0	0.953R1
5	0.20	63.0	38.9	50.6	10.5	0.950R1
6	0.04	58.0	42.2	57.1	0.7	0.960R1
7	0.01	56.5	43.4	56.5	0.1	0.950R1

a radius of the circle containing the casein and air components

CHAPTER 9
NUCLEAR MAGNETIC RESONANCE STUDIES ON CASEINS

9.1. INTRODUCTION

The physical state of the water in biological materials may have a major influence on their quality and stability. Water in biological samples may be described as either unbound or bound (Williams-Gardner, 1971). Bound water is the portion that is closely associated with the material and thus shows physical properties different than those of free or bulk water (Kuprianoff, 1958). Leung *et al.* (1976) have enumerated several methods of determining bound water in foods. They were primarily based on dehydration, calorimetry, electrical properties, solvent properties, infrared spectroscopy and nuclear magnetic resonance (NMR).

Pulsed NMR has become one of the most important techniques for studying the binding of water in biological macromolecules. Detailed information about the technique of pulsed NMR can be found in Farrar and Becker (1971), and the important points are summarized in Section 9.2.

This technique is useful in measuring quantities such as nuclear spin relaxation times and self diffusion coefficients (D) of water in the sample (see Walter & Hope, 1971). These quantities are sensitive to molecular motion and can be used to assess the mobility of different fractions of water molecules which are partially immobilized by the substrate. There are two types of relaxation times, the transverse (T_2) and longitudinal (T_1) times. These are also known as the spin-spin (T_2) and spin-lattice (T_1) relaxation times.

Pulsed NMR has been used to study the state of water in protein-water systems including gelatin (Labuza & Busk, 1979; Maquet *et al.*, 1984), meat (Nakano & Yasui, 1979), milk (Brosio *et al.*, 1984), egg (Goldsmith & Toledo, 1985) and various proteins (Lambelet *et al.*, 1988). These studies reported the dependency of relaxation times on the moisture content of the sample, however no data on the self diffusion coefficient of water were included. Two papers reported T_2 values of adsorbed water on dried casein (Brosio *et al.*, 1984; Leung *et al.*, 1976). Studies on the self diffusion coefficient of water as a function of moisture for starch/water systems (Lechert *et al.*, 1980; Lechert, 1981) and protein/water systems (Back *et al.*, 1991) have been published.

9.2. MEASUREMENTS OF THE T_2 and D VALUES

The NMR signal derives from the magnetic moments of the protons present in the sample. The protons are excited by very short pulses (90^o and 180^o), which are bursts of radio frequency (RF) power whose intensity and duration are adjusted so that the macroscopic nuclear magnetic moment is rotated respectively through 90^o and 180^o with respect to the external magnetic field.

When a 90^o pulse is applied at time t=0 a free induction decay (FID) curve is generated. By applying a 180^o pulse at $t=\tau$, the signal is refocused to form a spin echo at $t=2\tau$ (Figure 9.1). In the absence of diffusion the spin echo amplitude decays as,

$$E = E_o \exp(-2\tau/T_2) \tag{9.1}$$

where: E = spin echo amplitude
E_o = amplitude of the free induction decay curve at t=0
T_2 = transverse relaxation time

In the presence of a magnetic field gradient the spin echo is attenuated by molecular diffusion. This enables the self diffusion coefficient (D) to be measured using the pulsed gradient spin echo technique (PGSE) (Stejskal & Tanner, 1965). Hence an external field gradient (G) is imposed using a gradient coil, with current pulses of width (δ) and separation (Δ) (see Figure 9.2). For isotropic, unrestricted diffusion the attenuated spin echo (E') is given by the reduced form of the Stejskal and Tanner equation,

$$E' = E \exp[-\gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \tag{9.2}$$

where: γ = proton gyromagnetic ratio (2.675×10^8 $T^{-1} s^{-1}$)
G = external magnetic field gradient (1.18 T m^{-1} A^{-1})

For the experiments in obtaining D, the values of τ, Δ and G are chosen (usually $\Delta = \tau$). The gyromagnetic ratio is the same for all measurements. The values of E' are recorded for a range of δ values from 0 to δ_{max} ($<\tau$). By plotting ln (E'/E) against [δ^2 (Δ - δ/3)] the self diffusion coefficient is obtained from the slope of the regression line.

The spin echo signal is recorded, commencing at $t=2\tau$ and Fourier transformed to yield the echo spectrum. The apparatus is based on a commercial 60 MHz high-resolution

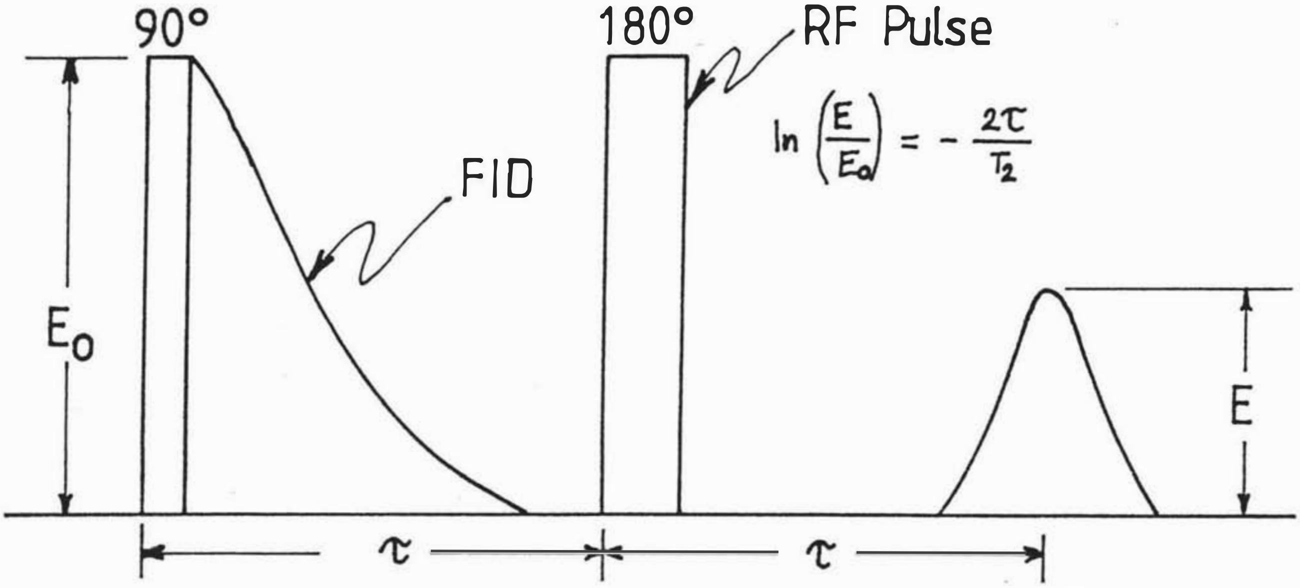


Figure 9.1. Radio frequency (RF) pulse sequence for the spin echo experiment to determine the transverse relaxation time (T_2).

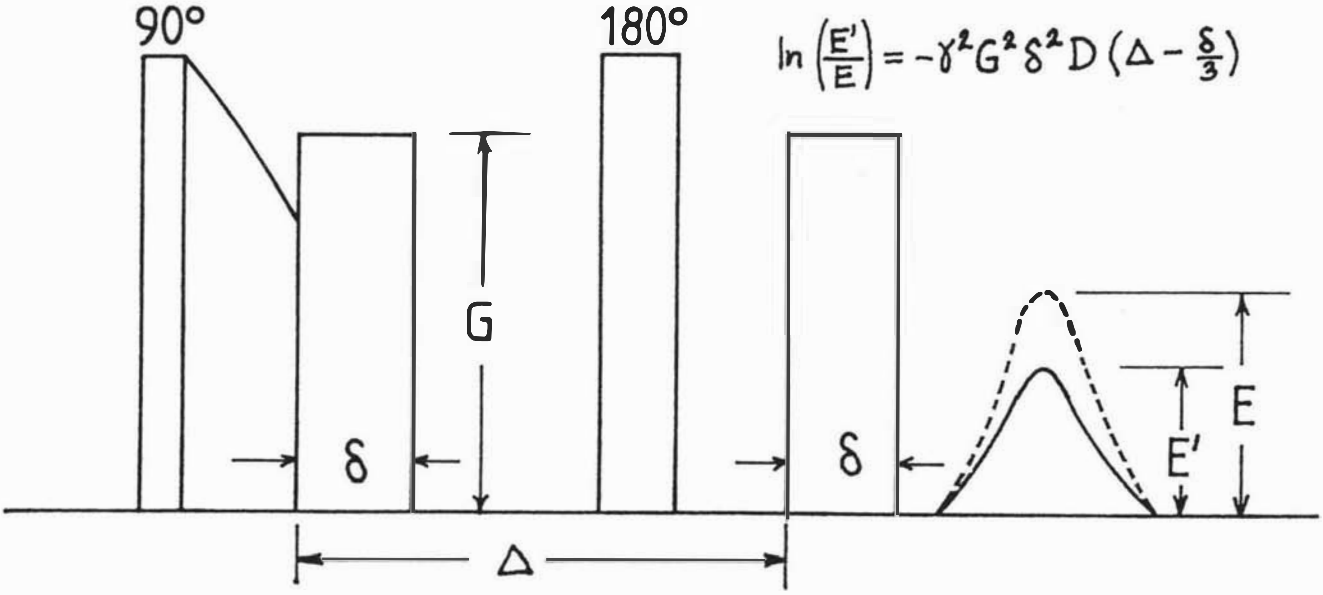


Figure 9.2. Field gradient pulse sequence for the attenuation of the spin echo to determine the self diffusion coefficient (D).

pulse-Fourier transform spectrometer (Section 3.2.3). For this instrument and for the drier samples (MC < 0.40 kg water/kg DS) a small signal from the solid casein could partially be resolved from the water proton signal (width = 1 kHz).

9.3. SELF DIFFUSION COEFFICIENT OF WATER IN CASEINS

Figure 9.3 shows the plots of self diffusion coefficient against moisture content for different types of casein. At the lowest moisture concentrations measurements were ultimately limited by: a) diminishing water signal; b) the need for higher gradient currents at lower diffusion coefficients (with a maximum of 10 Amperes available); and c) rapidly decreasing T_2 (as described below) and consequent limitation on τ and δ_{max}. In practice only samples with MC > 0.30 kg water/kg DS could be measured.

For all types of casein the self diffusion coefficient increased with an increasing moisture content. The rennet casein appeared to have slightly higher self diffusion coefficients than the acid caseins; however the D values are within the error bars of the acid caseins except for the D at the highest moisture. The maximum self diffusion coefficient of water in the caseins was about 25% that of free water (2.27×10^{-9} m^2/s at 25^oC; Mills, 1973). This lower value for D is due to the obstruction effect of hydrated macromolecules (see Walter & Hope, 1971).

The same dependency of D with moisture content has been observed for water in other macromolecular systems: Lechert *et al.*, (1980) and Lechert (1981) for starch/water systems and Back *et al.*, (1991) for protein/water systems. These results can be characterized by a simple model in which the water molecules can occupy two different sites: a) a 'bound' or immobilized site, probably attached to the protein molecules; and b) a 'free' or 'unbound' site, with properties approaching those of bulk water. This model was first introduced by Zimmerman and Brittin (1957) to describe the transverse relaxation of water in silica gel.

Karger *et al.* (1988) have examined self diffusion of adsorbed water, using this model for extreme cases:

a) where the two sites are isolated the Stejskal-Tanner plot of Equation 9.2 yields a sum of exponential decays with diffusion coefficient, D_i; and
b) where molecules undergo exchange between the two sites, on a time scale which is much shorter than the measurement time (ms), the resulting diffusion coefficient is the average of the values D_i for the different sites, weighted according to the probability (P_i) of site occupancy,

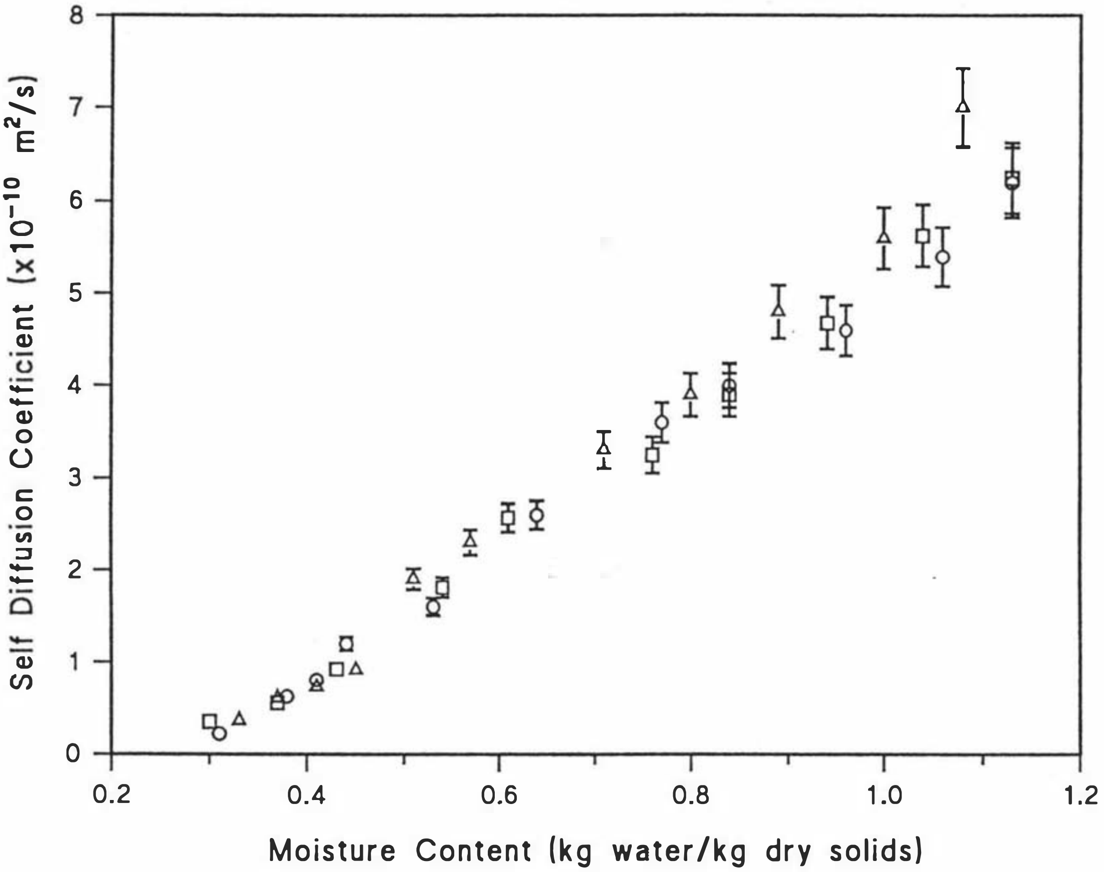


Figure 9.3. Self diffusion coefficient (D) against moisture content for rennet casein (△), mineral acid casein (○) and lactic casein (□) dried in a fluidized bed drier at 81°C, air velocity of 1.6 m/s and at ambient humidity. Bars indicate 95% confidence bounds on the mean values.

$$D_{ave} = P_1 D_1 + P_2 D_2 \qquad (9.3)$$

where: P_1 = probability of occupancy in the bound site
D_1 = self diffusion coefficient in the bound site
P_2 = probability of occupancy in the unbound site
D_2 = self diffusion coefficient in the unbound site
$P_1 + P_2 = 1$

In this model the diffusion coefficients reflect the molecular mobility of the various sites, with $D_1 = 0$ for the bound site, and D_2 close to that of bulk water. The relative site occupancies P_1 and P_2 will depend on moisture content. For MC < 0.30 kg water/kg DS it is clear from Figure 9.3 that all water is bound and $P_2 = 0$, for MC > 0.30 kg water/kg DS the amount of free water, and hence P_2 increases steadily.

The amount of bound water, as obtained from Figure 9.3, can be compared with results obtained from the sorption measurements on caseins (Section 4.1). Kuntz and Kauzmann (1974) have shown that the amount of hydration for different proteins from NMR measurements can be correlated with the sorption measurements at a_w near the saturation pressure of water. By extrapolating the fitted equations for caseins at 27-28^oC (Section 4.1.2), the moisture contents near the saturation pressure (a_w=0.99) for the mineral acid, lactic and rennet caseins were 0.304, 0.295 and 0.281 kg water/kg DS, respectively with a mean of 0.293 kg water/kg DS. The maximum moisture level for bound water can also be determined from the plot of heat of sorption against moisture content; i.e. from the point when the heat of sorption equals the heat of vaporization of water (Soekarto & Steinberg, 1981). From Section 4.4, this point occurred at 0.27-0.30 kg water/kg DS which again compares well with the value obtained from Figure 9.3.

Ruegg *et al.* (1974) reported that the amounts of unfreezable water for micellar, rennet and acid caseins were similar and had a mean of 0.43 kg water/kg DS. The unfreezable water can be interpreted as the bound water in the sample (Kuprianoff, 1958). The higher value obtained in terms of unfreezable water might be experimental error, because the accuracy of the scanning calorimeter is considerably reduced by the poorly defined limits of desorption, and perhaps by the lack of complete thermal equilibrium at each temperature (Kuntz & Kauzmann, 1974). However the data showed that there was no difference observed in amount of bound water for the different types of casein, in agreement with the results presented here.

9.4. RELAXATION OF WATER IN CASEINS

9.4.1. Transverse Relaxation Time

Investigations on biological materials using pulsed NMR can be carried out by determining either the T_1 or T_2 relaxation times of water protons. T_2 has been found to be a better tool for studying polysaccharides (Child & Pryce, 1972) and proteins (Lambelet *et al.*, 1988; Maquet *et al.*, 1984). Because of the different relaxation rates in the various water environments T_2 can also be an indicator of the strength of water binding in macromolecules (Leung *et al.*, 1976). Therefore T_2 measurement is highly dependent on the bound water fraction present. This is in contrast to the diffusion experiments which examined preferentially the unbound water component.

Figure 9.4 shows plots of T_2 against moisture content for different types of casein. The T_2 values for each casein were obtained from the plot of the spin echo decay as a function of pulse spacing (spin echo decay curve). Figure 9.5 shows the plots of the logarithm of echo height against pulse spacing for lactic casein with different moisture content. For τ values shorter than about 250 µs echo amplitudes were uncertain due to RF pulse ringing. At longer times, the water signal became obscured by other, partially overlapping signals from protons associated with the solid proteins (with $T_2 > 20$ ms). The T_2 data for the acid caseins were very similar, and were much higher than that for rennet casein. The slope of the plot for the rennet casein is only about a third that for the acid caseins. This is further demonstrated in Figure 9.6 showing the spin echo decay curves for the three types of casein at comparable moisture contents. For all types of casein, T_2 decreased with decreasing moisture content. This is consistent with the multiple-site environment with rapid exchange between sites, in which T2 is an average of possible sites, weighted according to site occupancy (Zimmerman & Brittin, 1957). The values for acid caseins compare well with the data reported by Leung *et al.* (1976) for casein measured at 10 MHz. The same trend of results were also reported by Lambelet *et al.* (1988) for gelatin, whey, egg white and soya proteins, and Brosio *et al.* (1984) for milk proteins (albumin, γ-globulin and casein). Nakano & Yasui (1979) suggested that the removal of water during drying immobilizes the inner hydration layers and therefore shortens T_2. This explained their results on dehydrating myosin suspension in P_2O_5.

The T_2 value for pure water at 20 to 25°C is about 3 seconds (see Walter & Hope, 1971) which is about 200 and 750 times that of the maximum T_2 for acid caseins and rennet casein, respectively. The very low values of T_2 could be attributed to the rapid exchange of water molecules between the two states of water (unbound and bound water). For all samples, the decay of the water spin echo was found to be described by a single

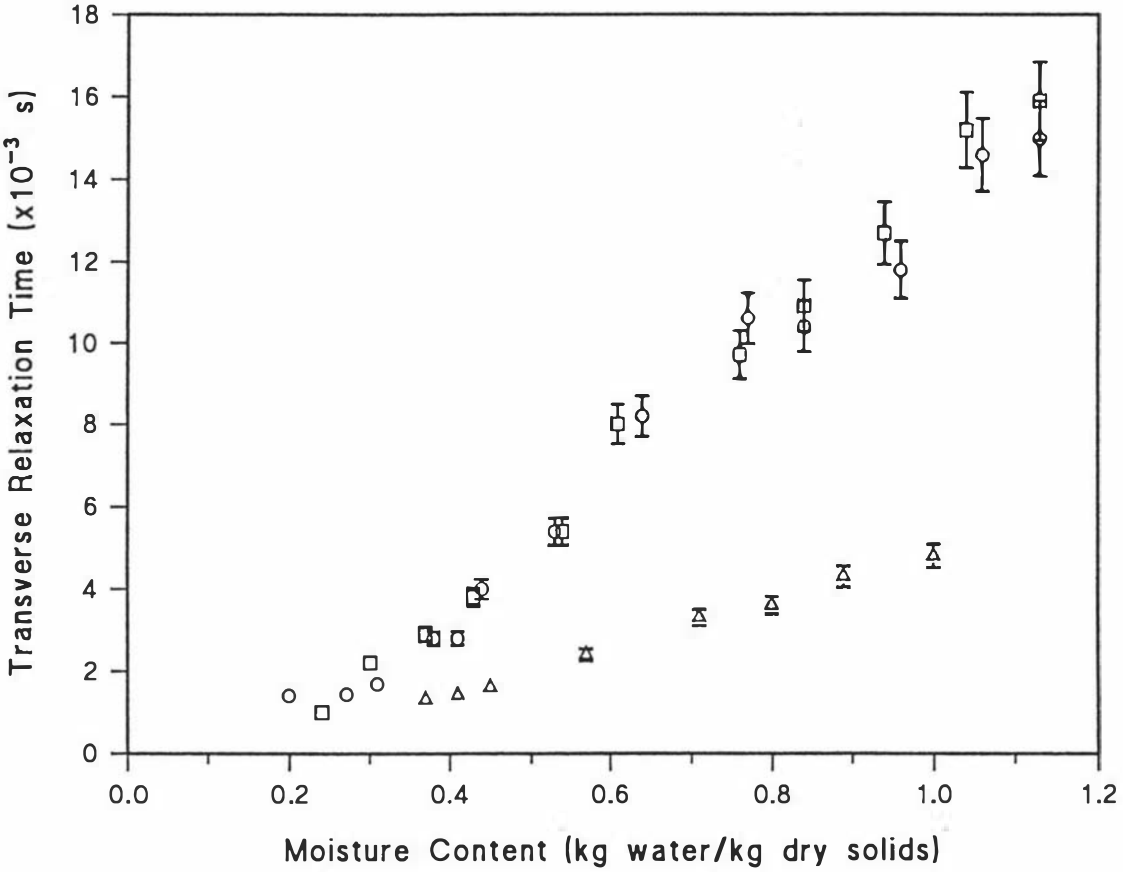


Figure 9.4. Transverse relaxation time (T_2) against moisture content for rennet casein (△), mineral acid casein (○) and lactic casein (□) dried in a fluidized bed drier at 81°C, air velocity of 1.6 m/s and at ambient humidity. Bars indicate 95% confidence bounds on the mean values.

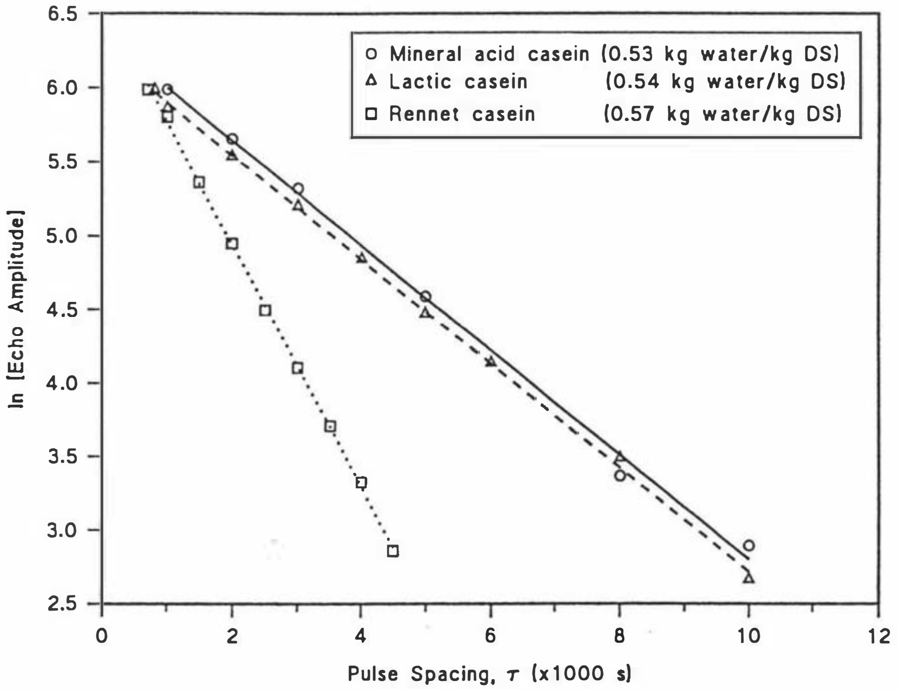


Figure 9.6. Echo decay curves for mineral acid casein, lactic casein and rennet casein at approximately similar moisture content and dried in a fluidized bed drier at 81°C, air velocity of 1.6 m/s and at ambient humidity.

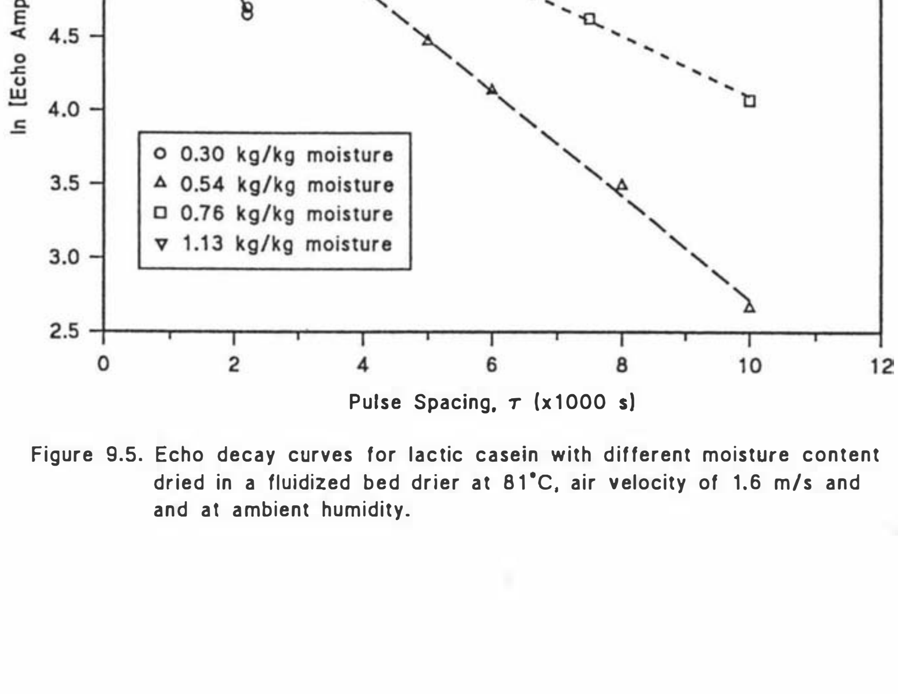


Figure 9.5. Echo decay curves for lactic casein with different moisture content dried in a fluidized bed drier at 81°C, air velocity of 1.6 m/s and and at ambient humidity.

exponential decay (Figures 9.5 & 9.6). Again this is consistent with the characterization of the water as undergoing rapid exchange between sites.

9.4.2. Differences Between Acid and Rennet Caseins

While the diffusion results for the three caseins were very similar, the T2 results were markedly dependent on the casein type. These differences can be reconciled by referring to the 2 site model with rapid exchange.

The average T_2 (T_{2ave}) is obtained from the relaxation rates of the various sites, with appropriate weightings to give (Zimmerman & Brittin, 1957),

$$1/T_{2ave} = P_1/T_{21} + P_2/T_{22} \qquad (9.4)$$

where: T_{21} = transverse relaxation time in the bound site
T_{22} = transverse relaxation time in the unbound site

For the unbound site, T_{22} will be close to that of free water which is long, since local dipolar fields are averaged to zero by the rapidly tumbling molecular motion. The term P_2/T_{22} is therefore negligible compared to the first term in Equation 9.6. However, for the bound site the relaxation rate in the temporarily immobilized molecule will be much more rapid. Thus the T_2 results reflect more strongly the nature of the bound water. There is therefore a need to examine in detail factors which may influence either site occupancies (P_i) or the site relaxation rates ($1/T_{2i}$).

From both diffusion and sorption measurements, the bound water fraction for the three caseins were similar. However, the relaxation rates in the bound sites may be sensitive to additional mineral content or other compositional differences in the rennet casein. In the precipitation of acid caseins, the aggregation of casein micelles is promoted by reducing the nett negative charge on the casein micelles to near zero by reducing the pH to the isoelectric point of 4.6. For rennet casein, the negative molecular charge is reduced to near zero by enzymic removal of the negatively charged tail from the κ-casein molecule. The removal of the glycomacropeptide which is the most hydrophilic grouping of the casein complex (Ruegg *et al.*, 1974) leaves a more hydrophobic rennet casein surface. The calcium phosphate is not made soluble, so the ash content of rennet casein is high. Acid caseins typically contain 1.8% ash and rennet casein typically contains 7.8% ash. It is likely that this extra mineral in rennet casein would bind water tightly. Removal of the hydrophilic κ-casein tail presumably also contributes to stronger water binding in the remaining casein. The D and T_2 values therefore follow different trends because in the above model relaxation in the bound state (T_2) does not influence the water mobility in the unbound state (D).

The above discussion is based on a general model in which the parameters (T_2 or D) are weighted according to the relative occupancy of available sites. Such a model has been applied successfully to a variety of food materials and other substances. Further work is required in order to shed light on the detailed nature of the water binding to the casein molecules.

9.5. MOISTURE EQUILIBRATION OF CASEIN PARTICLES

Figure 9.7 shows a plot of self diffusion coefficient at 20 minute intervals immediately after leaving the drier for mineral acid casein particles. The sample analyzed had a moisture content of about 0.33 kg water/kg dry solids which is a little above the maximum bound water fraction (Section 9.3). The self diffusion coefficient decreased with an increased in time. It took about 200 minutes for the D value to equilibrate at a constant value of about 0.6×10^{-10} m^2/s. This is in good agreement with the D value at a moisture level at 0.36 kg water/kg dry solids in Figure 9.3. The equilibration time also compares well with the equilibration time of 180 minutes for moisture transfer between various sizes of dried casein obtained in Section 7.3.2.

The particles immediately after removal from the drier would have an inhomogeneous distribution of moisture, with a higher concentration at the particle centres, and more moisture in big particles than in small particles. The equipment measured a weighted average value for the diffusion coefficient over all the particles in the sample. As the moisture diffuses through the casein particles and between casein particles the average diffusion coefficient decreases to some equilibrium value because much of the unbound water in the centre of the particles diffuses into dry outer regions of the particles where it is tightly bound, and similarly unbound water in large particles diffuses into dry smaller particles. The sample particles used had a size range of d = 0.5 to 1.0 mm. Larger particles were not used because this would increase the space left in between the particles. The mean diffusion path (X) in three dimensions for a spherical particle is,

$$X = \sqrt{6 D t_D} \qquad (9.5)$$

where: t_D = diffusion time

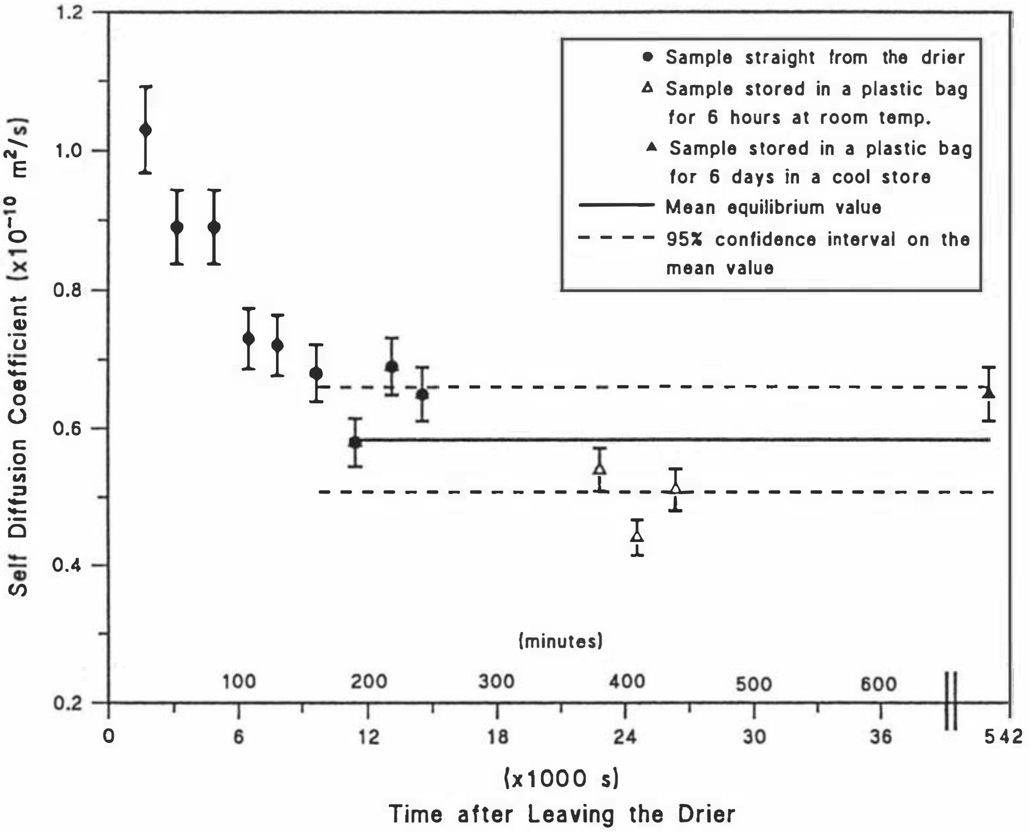


Figure 9.7. Self diffusion coefficient against time after leaving the fluidized bed drier at 81°C, air velocity of 1.6 m/s and at ambient humidity for mineral acid casein with 0.33 kg water/kg DS.

Using Equation 9.5, when $D = 0.6 \times 10^{-10}$ m^2/s (equilibrium value from Figure 9.7), and $X = d/2 = 0.25$ mm, $t_D = 3$ minutes; for $X = 0.5$ mm, $t_D = 12$ minutes. This shows that the equilibration time for moisture within the particles is about quarter of an hour or less for the particle size considered. The major barrier to moisture transfer in this experiment is therefore presumably the air gaps and contact area between particles rather than diffusion within the casein particles.

9.6. NMR IMAGING OF CASEIN

9.6.1. Background

Nuclear magnetic resonance imaging (NMRI) is a relatively new field of investigation first proposed independently by Lauterbur (1973) and Mansfield and Grannel (1973). The theory and technique of NMRI can be found in Morris (1986) and Callaghan (1991). An NMR image represents a 'slice' through the sample and is a spatial map derived from the NMR responses of mobile molecules, usually water or lipid. The variation in image intensity and hence the contrast arises from differences in the concentrations of mobile protons or differences in the relaxation rates of the nuclear spins.

The year 1986 ushered the beginning of NMRI for practical applications in biological systems. Proton density maps at a spatial resolution corresponding to a voxel size smaller than $(0.1 \text{ mm})^3$ have been reported using the NMRI by several groups of investigators (Aguayo *et al.*, 1986; Eccles & Callaghan, 1986; Lauterbur, 1986). Recently, applications of NMRI to foods have been reported by Duce *et al.* (1990) for chocolate bars and by Reid and Litchfield (1991) for apples and potatoes, and corn during drying (Song & Litchfield, 1990).

9.6.2. Proton Images of Casein

The results presented in this section had been published as part of a paper entitled 'Some biophysical applications of motional contrast in n.m.r. microscopy' (Back *et al.*, 1991).

Figure 9.8 shows the proton image for a 55% moisture (w.b.) (1.22 kg water/kg DS) mineral acid casein particle with a mean diameter of 3 mm obtained using static NMR imaging. The echo delay time between slice excitation and image formation was 6 ms and the total image acquisition time was 40 minutes (Figure 9.8a). Two other images with echo decay times of 12 and 20 ms were also obtained so that the effect of

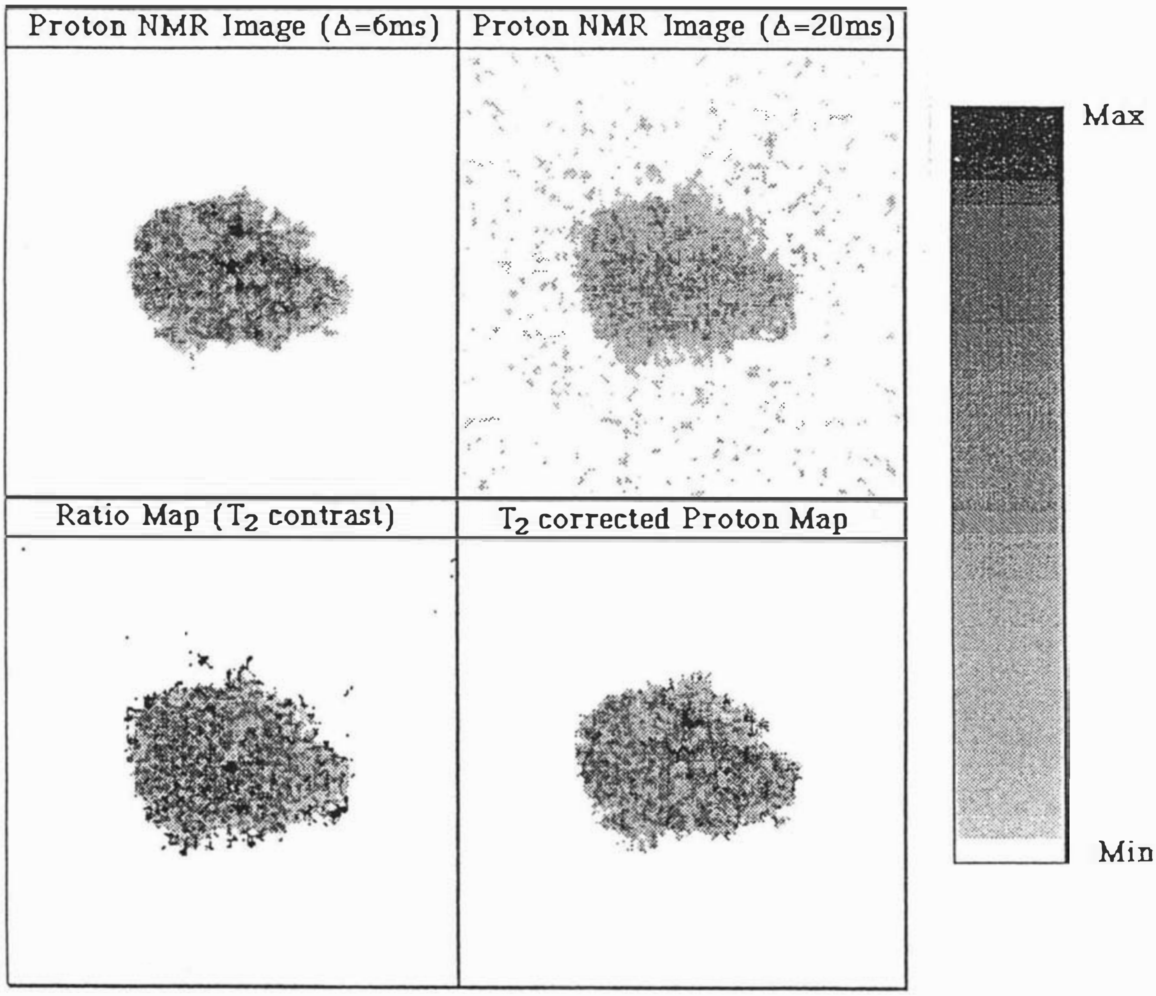


Figure 9.8. Proton images of a wet mineral acid casein particle with 1.22 kg water/kg DS moisture content (static imaging). All the images have the same intensity scale. The three proton maps show higher moisture content for darker shading. For the ratio map, the darker shading represents a longer T_2.

relaxation (with bulk T_2 of order 15 ms) in attenuating the image could be assessed. The 20 ms image is also shown for comparison in Figure 9.8b. Consistent images were obtained at intervals over 24 hours indicating an equilibrium moisture distribution in the bulk particle. A T_2 contrast image was obtained by taking a ratio of the 6 ms and 20 ms images (Figure 9.8c). Variations in T_2 were observed with shorter values along the outer regions. Assuming a single exponential decay (Section 9.4.2), the 6 ms image was extrapolated back to t=0 to obtain the relaxation corrected proton density map (Figure 9.8d). Figure 9.8d shows that there are regions within the particle with high moisture content and possibly some air gaps (shown as very low intensity). These results confirm the observations in Section 8.3.1 where a wet mineral acid casein particle was found to contain a considerable air pore volume (approximately 40% of the total particle volume).

Using dynamic NMR imaging the self-diffusion map for the particle is obtained and shown in Figure 9.9a. Using the casein diffusion/moisture dependence of Figure 9.4 a moisture image may be calculated as shown in Figure 9.9b. The results can be compared with the image in Figure 9.8d. Observations noted in Figure 9.8d were similar to those shown by Figure 9.9b. Figure 9.9a shows higher water diffusion near the edges of the particle. This is also the region where shorter T_2 values were observed. With the exchange model used to derive the water density image from the distribution of D values, both T_2 and D are expected to be similarly dependent upon moisture content, shown in Figures 9.3 and 9.4. It is therefore not appropriate in this case to depict the higher D value as arising from higher moisture content since then we would expect T_2 values to be also increased. In consequence the calculated proton map (Figure 9.9b) is misleading.

This inverse dependence of T_2 and D can be attributed to magnetic susceptibility effects as pointed out by Back *et al.* (1991). They reasoned that because a large scale structural variation was observed it is possible that a slow fluctuation regime exists which would explain the inverse relation between apparent relaxation time and local D. Because of this slow-motion susceptibility effect, the assumption of the relaxation of the form $\exp(-t/T_2)$ is not justified and extrapolation to t=0 is difficult. Hence the results from these imaging experiments is insufficient for one to draw conclusions regarding moisture distribution without additional experiments to clarify the effects of susceptibility variations within the sample.

Attempts were made to measure the moisture distribution in a partly dried casein particle immediately after removal from the drier. However, moisture equilibration was too rapid for the higher moisture content in the middle of the particle to be

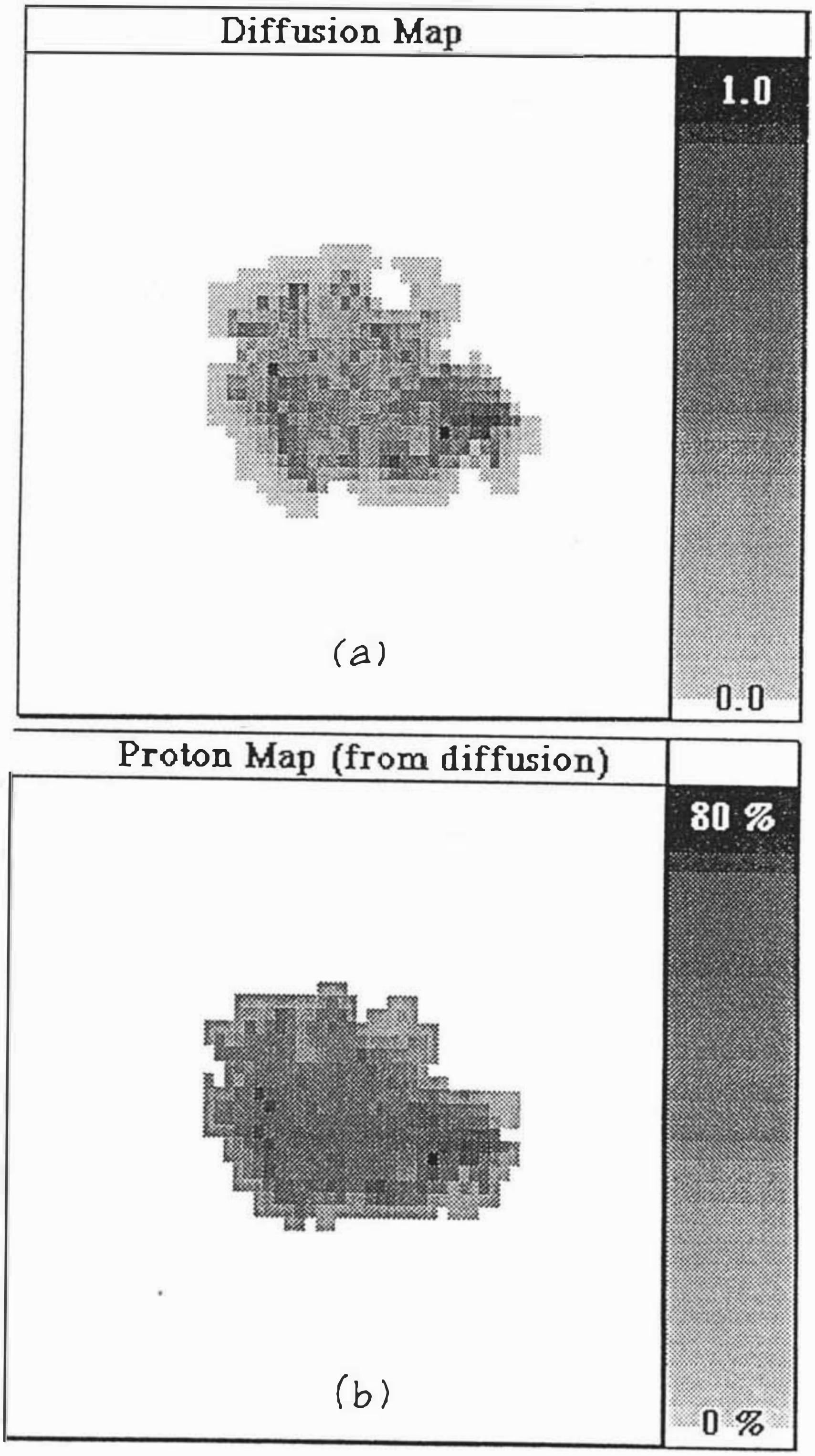


Figure 9.9. Proton and diffusion maps of a wet mineral acid casein particle with 1.22 kg water/kg DS moisture content (dynamic imaging). The scale for the diffusion map has units 10^{-9} m^2 s^{-1}, while the scale for the proton map has units % relative water density.

measured, as might have been expected from the calculations in Section 9.5. If a 3 mm mean diameter casein particle with 0.33 kg water/kg DS moisture content is considered moisture redistribution within the particle is attained in less than two hours (1.74 hours).

Dynamic mapping of T_2 of a partly dried casein particle may be possible since much shorter times are required. This measurement would yield indirect information about the dynamic water distribution because of the similar dependence of T_2 and D values on moisture content. This experiment is currently being planned by the NMR group of the Department of Physics and Biophysics, Massey University, and is likely to proceed in the near future.

CHAPTER 10
THERMAL SENSITIVITY EXPERIMENTS ON CASEIN

10.1. INTRODUCTION

Drying is one of the most energy intensive processes in casein manufacture. The costs of casein manufacture and the quality of the product depend on the conditions under which the drier is operated. The higher the inlet drying temperature the higher the efficiency and capacity of a drier. However during the falling rate period the surface temperature of casein particles approaches the air drying temperature (Brennan *et al.*, 1976). Reactions occurring during drying can result in quality losses, particularly nutrient losses, and in other deleterious changes caused by non-enzymatic browning (Karel, 1975). For casein an increase in temperature may result in denaturation which may cause undesirable colour changes and insolubility in alkali.

Colour is an important quality parameter used for evaluating food products (Kramer & Twigg, 1970), and casein powders are no exception (BSI, 1963; USDA, 1968). Colour changes can be determined quantitatively using colorimeters. The most popular of these colorimeters is the Hunter designed instruments which use the L-a-b colour values for describing the colour of foods because it gives direct values on uniform, visually meaningful scales (MacKinney & Little, 1962). The Hunter L-a-b system employs a three dimensional colour solid with +L=white, -L=black, +a=red, -a=green, +b=yellow, -b=blue and zero=gray (Appendix 10.1). These three colour values are usually combined in some way to describe the colour index of the product, e.g. for processed tomato juice, the colour index = L b/a (Francis, 1975a). Instrumental methods for the colour evaluation of casein have been proposed (Seakins, 1971; Southward, 1978).

Solubility of casein in alkali is another important physical property of casein. The Borax test is the most common procedure for determining the solubility of casein in alkali (Sutermeister, 1939; Spellacy, 1953; BSI, 1963; NZDB, 1976). However Roeper (1975) has shown that there are some inconsistencies in the Borax test. He reported that the use of 0.5M sodium hydroxide for the solubility test gave better results. A standard method of reporting casein solubility in 0.5M sodium hydroxide is in terms of ml of insoluble matter per 10 g of casein used (Roeper, 1991). But the amount of casein used in the test depends on its moisture content, hence the solubility index was used in preference. Solubility index refers to the ratio of the ml of insoluble to the actual amount of dry casein used.

Jebson (1991) studied the moisture content-temperature-time relationship of lactic casein in terms of solubility and colour changes. He estimated from differentiation of the derived multiple regression equations on casein that the maximum thermal denaturation for pilot plant lactic casein was between 39 and 43% (w.b.) for insolubles and 32 and 46% (w.b.) for colour change. In order to design and operate efficient casein driers it would be advantageous to know the moisture content range where maximum thermal denaturation for other caseins occurs.

10.2. PRELIMINARY EXPERIMENTS

10.2.1. Factorial Experiments

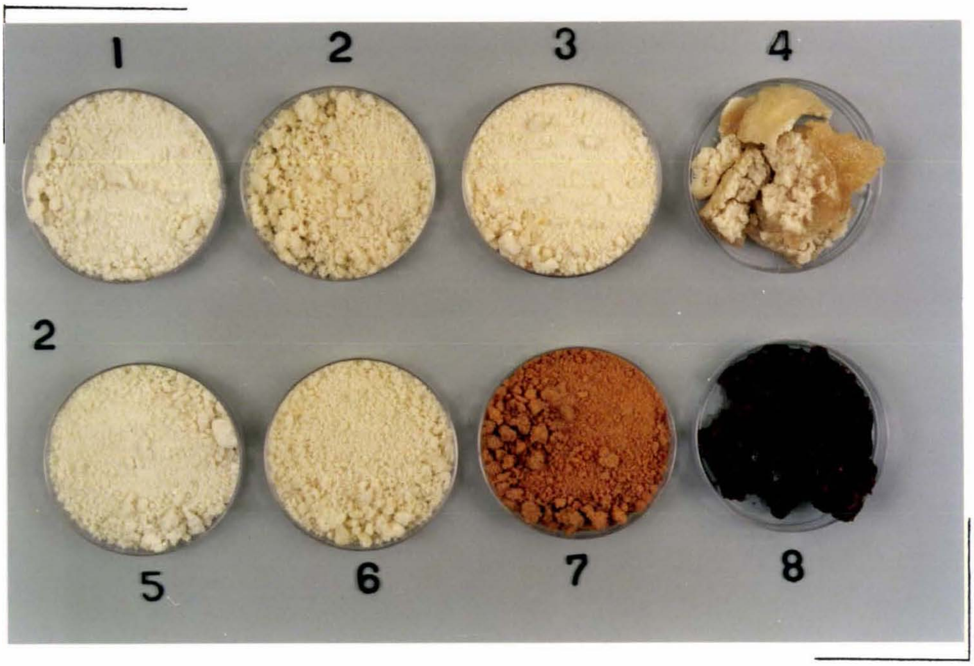
Factorial experiments on the thermal sensitivity of mineral acid casein samples were carried out at 60°C and 140°C, for two moisture contents and two holding times. Table 10.1 presents the solubility index and Hunter L-a-b colour values for these samples and the appearance of the unground and ground samples are shown in Figure 10.1. Comparison of the results with the control sample showed that the solubility indices of the low moisture samples were not affected by exposing to 60°C for up to 2 hours. The colour values of the low moisture samples were not affected by the storage temperatures and times except for the sample exposed to 140°C for 2 hours. However some apparently conflicting results for the samples stored at 140°C were observed. At a storage time of 1/3 hour, the high moisture sample gave a higher solubility index than the low moisture sample. A comparison of the unground samples 3 and 4 in Figure 10.1 shows that the high moisture sample fused together but nothing happened to the low moisture sample. However after both samples were ground it was difficult to determine the difference visually. But using the Hunter L-a-b colour values, the low moisture sample was found to be less greenish, yellowish and grayish than the high moisture sample. At a storage time of 2 hours, at 140°C the high moisture sample (8) gave a much lower solubility index than the low moisture sample (7). But the resulting unground and ground samples (Figure 10.1) showed significant colour change with severe blackening on the high moisture sample. Both samples smelled burnt after removal from the storage can, indicating that severe denaturation may have taken place. The high moisture sample melted and flowed like condensed milk after opening the can, but it soon solidified after cooling. Storage at 140°C for 1/3 hour gave a reverse trend of solubility index with moisture content. The results obtained from these experiments are difficult to explain without further investigations. However it was decided not to pursue this since the conditions used for the samples were not realistic in commercial practice. Instead a lower storage temperature was selected since 140°C was too high resulting in very severe denaturation.

Table 10.1. Solubility index and Hunter L-a-b values for mineral acid casein from the preliminary factorial experiments.

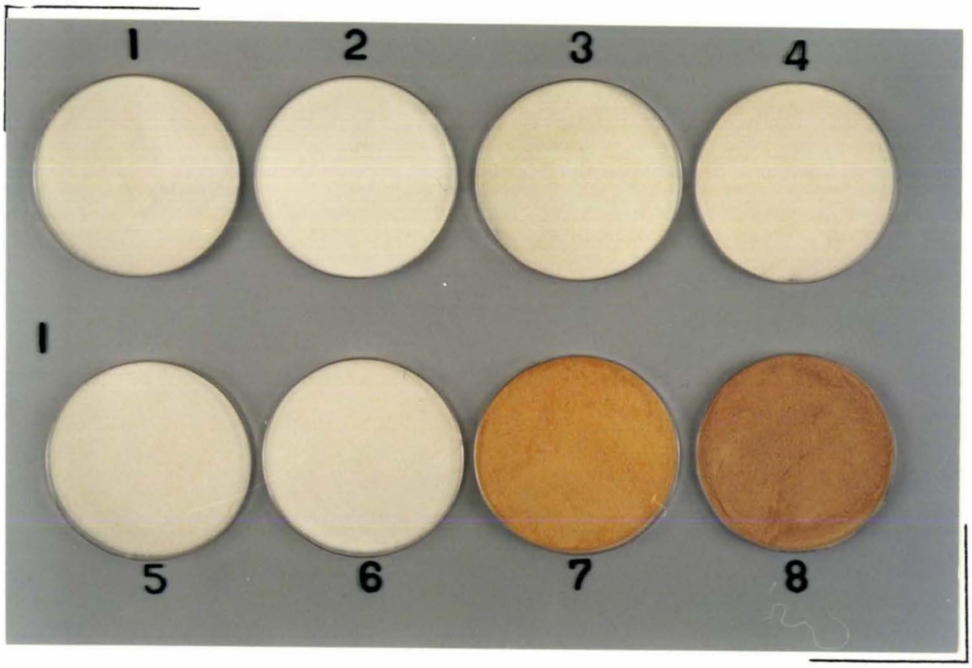
Sample Code	Storage Moisture Content (% w.b.)	Storage Temp (°C)	Storage Time (hour)	Test Moisture Content[c] (% w.b.)	Solubility Index[c] (ml insoluble/ g dry solids)	Colour Values[c] L	a	b
1	12	60	1/3	11.11	0.005	88.33	-1.96	6.44
2	51	60	1/3	5.84	1.008	88.27	-1.98	6.35
3	12	140	1/3	11.03	0.218	87.83	-2.03	7.58
4	51	140	1/3	6.02	2.185	84.72	-1.05	9.01
5	12	60	2	11.11	0.005	88.09	-1.92	6.27
6	51	60	2	5.39	1.627	87.27	-1.99	6.75
7	12	140	2	10.55	8.716	70.93	3.92	19.24
8	51	140	2	6.19	0.130	63.68	3.86	14.02
Control[d]	12	---	---	11.11	0.005	87.7±.8	-2.0±.1	6.5±.5

c average of 2 replications

d dried sample not exposed to any storage temperatures



a) Unground



b) Ground

Figure 10.1. Appearance of the ground and unground mineral acid casein from the preliminary factorial experiments.(see Table 10.1 for sample conditions).

10.2.2. Effect of High Storage Temperature on Casein

The effect of storage temperature on casein properties was studied in more detail. High and low moisture samples were exposed at storage temperatures of 140°C, 120°C and 100°C for 2 hours. The 140°C temperature was repeated to check the earlier observations. Figure 10.2 shows the plots of the solubility index against the moisture content of samples stored at different high storage temperatures for 2 hours. The solubility index for the high and low moisture samples stored at 140°C for 2 hours from the first test is also plotted in Figure 10.2 for comparison. At 100°C there was little change in the solubility index with moisture content. At the low moisture content, the solubility index rose sharply with an increase in storage temperature, while at the high moisture content, increasing the temperature reduced the solubility index, the effect being most noticeable at 140°C. Figure 10.3 shows the appearance of the ground samples stored at different high storage temperatures for 2 hours. The results indicate that severe colour changes occurred on all the samples at 120°C and 140°C but there was only a slight change on the samples at 100°C. It seems also that the high moisture samples had more severe colour changes than the low moisture samples at 120°C and 140°C. Spellacy (1953) pointed out that temperatures employed in the drying process will not materially affect the solubility of casein, provided they are not excessive and are properly correlated with air volumes. Burnt or scorched casein is rendered insoluble. The results have shown that this is the case for low moisture samples. However the results for the high moisture samples were surprising. The thermal denaturation reaction seems to be different because of the presence of a large amount of moisture which cannot evaporate during the heating process. Therefore these conditions are different from the drying of wet curd since the moisture will evaporate leaving the dehydrated casein solids. Hence 100°C was used as the high level storage temperature for the succeeding factorial experiments on casein because the trend of the results was similar to those found at 60°C.

10.2.3. Instrumental Colour Evaluations of Casein

The ground samples of casein from the factorial experiments in Section 10.2.1 were evaluated for their colour using the HunterLab Colorquest. The particle size of the samples were less than 500 µm. After several measurements it was found that the L-a-b values obtained were not reproducible. This was probably due to the wide size range of particle sizes making it difficult to achieve a uniform packing density. It was decided to grind the samples further to less than 250 µm thereby narrowing the size range. The packing density of the powder was much more reproducible, as were the resulting measurements of L-a-b values. In the succeeding experiments all samples

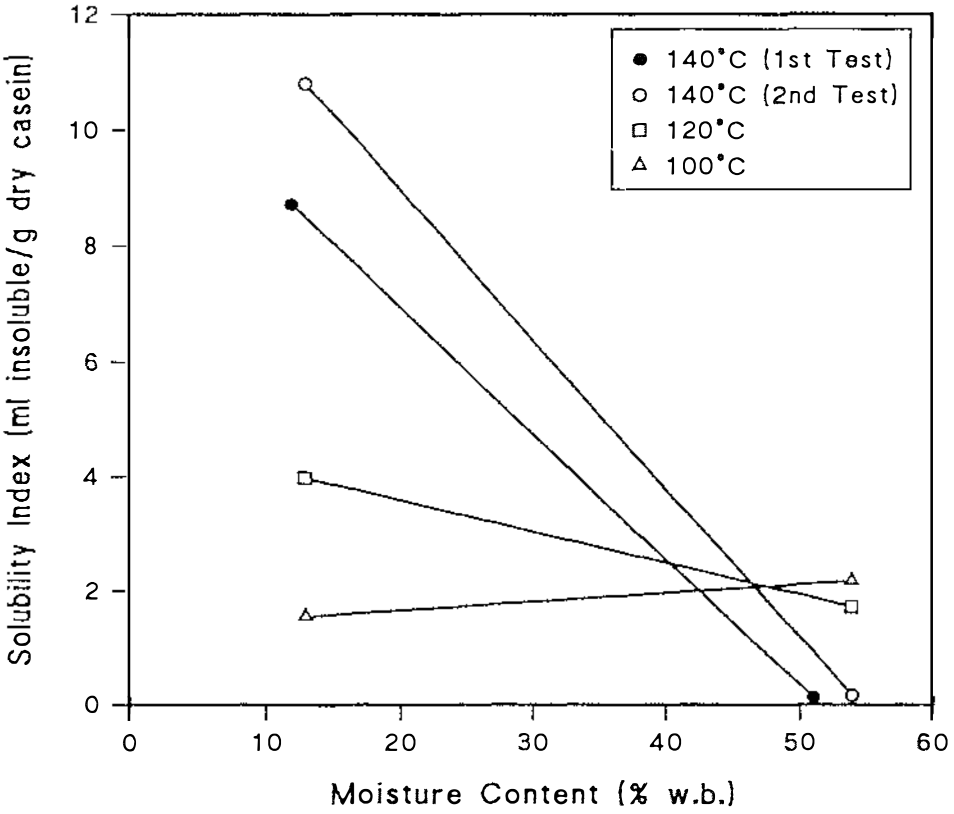


Figure 10.2. A plot of solubility index against moisture content of mineral acid casein held at different temperatures for 2 hours.

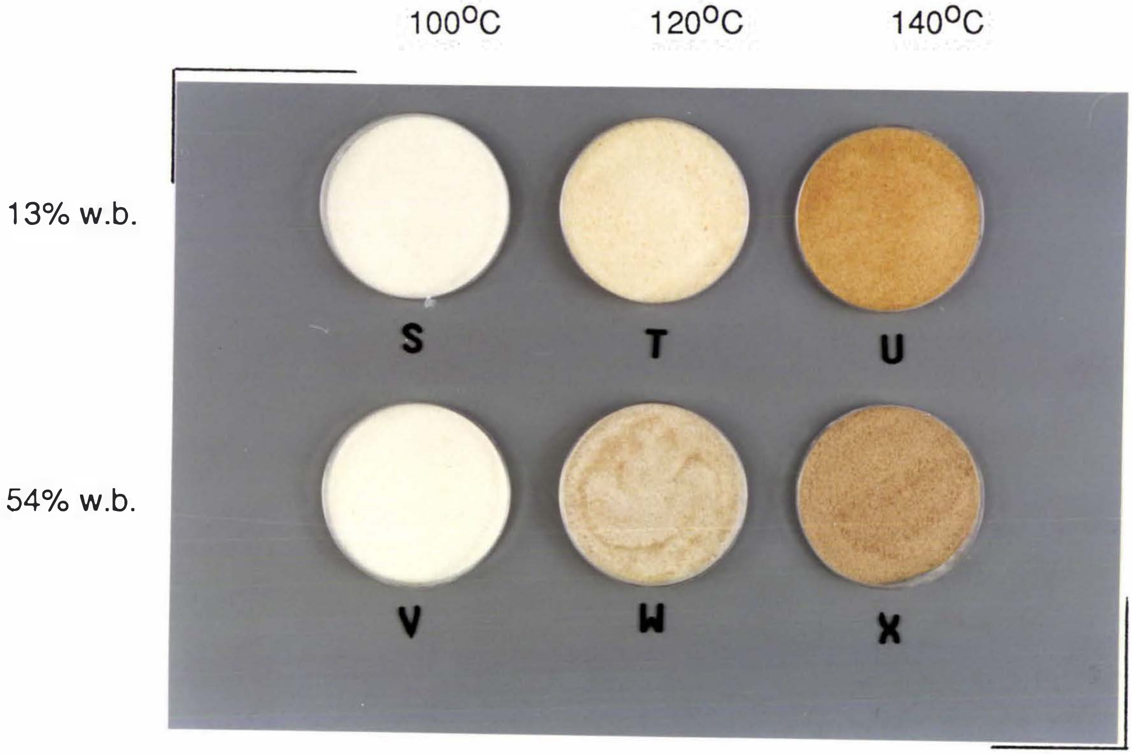


Figure 10.3. Appearance of the ground mineral acid casein stored at different high storage temperatures for 2 hours.

were ground to less than 250 µm for colour evaluations.

10.3. EXPERIMENTS ON WET AND DRY CASEIN

10.3.1. Effect of Moisture Content, Temperature and Time on Casein Solubility

10.3.1.1. Experimental Results

Table 10.2 summarizes the solubility index for the samples from another set of factorial experiments using 60°C and 100°C, two moisture contents and two holding times. The table also includes results of additional experiments at selected moisture contents, temperatures and times. The trend of the results for the storage of casein at 60°C confirmed the results found in Section 10.2.1. It is also interesting to note that the solubility index of wet casein increased significantly even if held at 60°C for only 20 minutes. The very high solubility index obtained for some samples was due to the swelling of insolubles which greatly increased the volume. Hadert (1938) also reported the swelling of casein insolubles when dissolved in a borax solution.

Figure 10.4 shows the effect of storage temperature and moisture content on solubility index of mineral acid casein held for 2 hours. As expected, the higher the storage temperature of casein the higher the solubility index at all moisture levels. However samples with an intermediate moisture content (30% w.b.) gave higher solubility indices than the low and high moisture samples and the effect became more significant at higher storage temperatures.

Figure 10.5 shows the effect of storage time and moisture content on solubility index of mineral acid casein held at 100°C. The longer the storage time the higher the solubility index at all moisture levels. The effect of increasing the time from one hour to 2 hours seemed to be less significant for the samples with high moisture content. Again the sample at intermediate moisture content had a higher solubility index than the low and high moisture samples.

Sutermeister (1939) reasoned that the solubility of casein in alkali is enormous as compared to acids due to the ionizing of the carboxyl groups by liberating it from the amino groups within the micelles. Hence the solubility of dried casein is less than that of freshly precipitated casein because the extent of internal neutralization of carboxyl and amino groups increases as the micelles are brought closer together by drying. In general the solubility of casein in alkali is decreased the lower the moisture content to

Table 10.2. Solubility index for mineral acid casein from the factorial experiments including the additional experiments on wet and dry samples.

Sample Code	Storage			Test Moisture Content (% w.b.)	Solubility Index (ml insoluble/ g dry solids)
	Moisture Content (% w.b.)	Temp (°C)	Time (hour)		
1	14	60	1/3	9.90^c	0.005^c
2	56	60	1/3	8.07^c	2.159^c
3	14	100	1/3	7.89^c	0.005^c
4	56	100	1/3	8.14^c	2.286^c
5	14	60	2	10.01^c	0.005^c
6	56	60	2	7.92^c	2.469^c
7	14	100	2	9.36^c	2.709^c
8	56	100	2	10.23^c	3.386^c
9	14	80	2	8.52	0.996
10	56	80	2	7.94	3.089
11	30	60	2	7.30	2.596
12	30	100	1/3	6.16	3.088
13	30	100	2	7.32	4.054
14	30	80	2	6.64	3.475
15	56	100	1	7.24	3.326
16	43	100	1	6.98	3.327
17	30	100	1	5.94	3.742
18	19	100	1	9.03	2.455
19	14	100	1	8.28	0.579
Control^d	14	---	---	7.77	0.005

c average of 2 replications

d dried sample not exposed to any storage temperatures

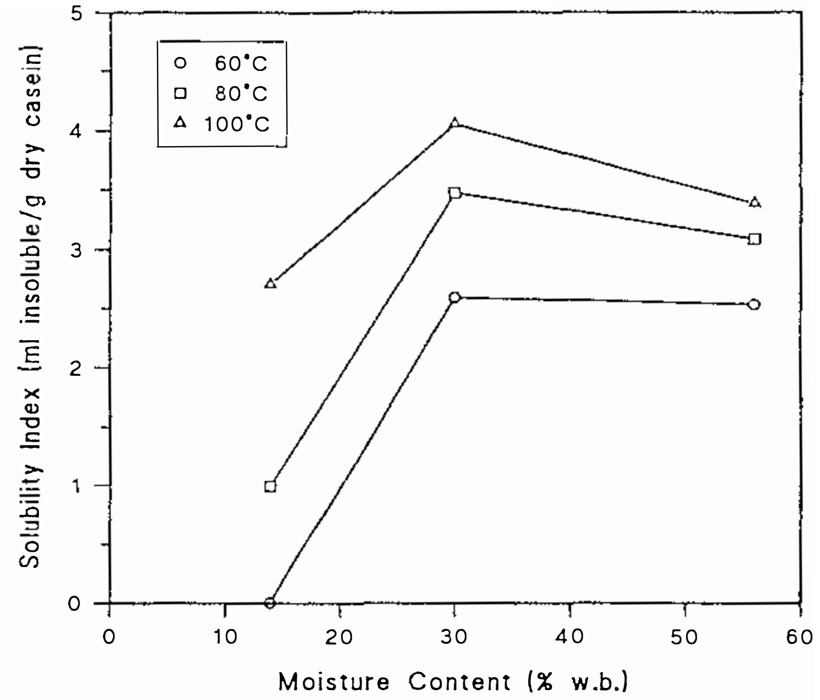


Figure 10.4. A plot of solubility index against moisture content of mineral acid casein held at different temperatures for 2 hours.

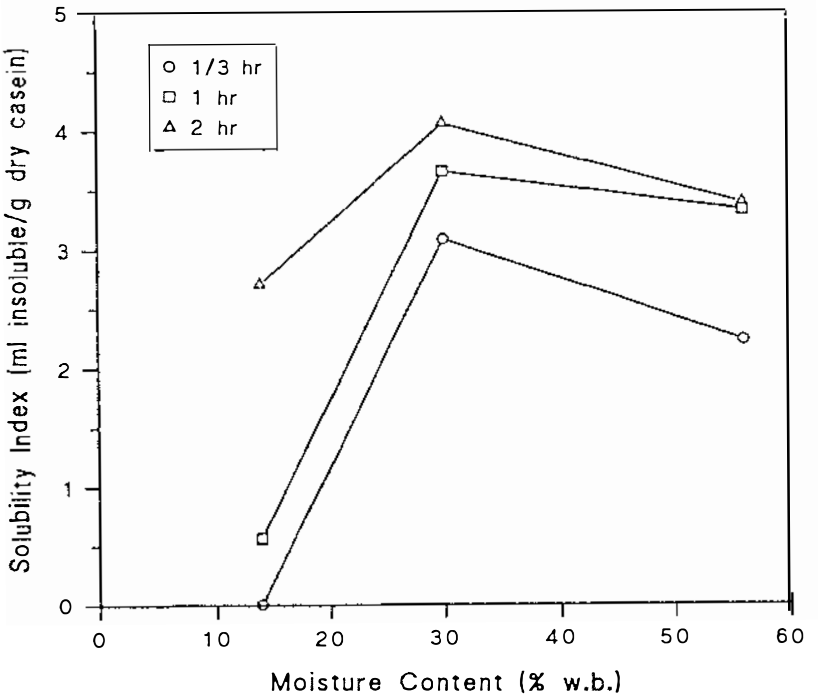


Figure 10.5. A plot of solubility index against moisture content of mineral acid casein with different storage time held at 100°C.

which casein is dried and the lower the temperature at which it is dried (Browne, 1939). Caseins exposed to high drying temperatures and long residence times had increased insolubility (Sutermeister, 1939).

Jebson (1991) postulated that the water present in casein has two roles in the reactions: a) as a solvent or more correctly diluent which allows some steps of the reactions to proceed more easily; and b) as a reactant. At high moisture contents there is probably more than enough water for both roles, and the excess would act as a diluent, reducing the concentration of the reactants and hence decreasing the reaction rate. At low moisture contents there is probably insufficient water for both roles, and particularly as a reactant. Therefore a moisture level in between these two extremes would be expected to maximize casein denaturation.

10.3.1.2. Multiple Regression Equations

The factorial experiments were duplicated to determine the important factors including interactions that affect the solubility index of casein. Two approaches were used. Firstly the method of Stoodley *et al.* (1980) was used to make F-test comparisons on the estimated effects. Secondly, the procedure of Caulcutt (1983) was used to make t-test comparisons on the estimated effects. Sample calculations for each of these procedures are found in Appendices 10.2 and 10.3. Both methods indicated that moisture content was ranked first followed by time, temperature, temperature-time interaction, moisture content-temperature-time interaction, moisture content-temperature interaction and moisture content-time interaction, respectively. It was also found that all factors including interactions were significant even at the 99.9% level. This is because of the very big variations of the solubility index from sample to sample. This point will be clarified in Section 10.5.2 in the factorial experiments on dry casein where variations in the solubility index were low.

Multiple regression equations were fitted to the results of the factorial experiments using the Minitab program (Ryan *et al.*, 1981). The first attempt was to regress the solubility index in terms of the first 4 factors/interactions in linear form mentioned above. The r^2 of this regression was only 62% which showed the inadequacy of the equation. It was noticed that the effect of moisture content on the solubility index was at least twice that of the next factor. Hence different relationships with moisture content were tried in the regression equation, i.e. logarithmic, exponential, quadratic and polynomial. It was found that the polynomial form gave the best result and was incorporated into the regression equation. The r^2 of the regression increased significantly to 95% showing a very good fit of the data (Appendix 10.4). The regression equation has the form,

$$SI = -7.438 + 0.772M - 0.019M^2 - 0.000147M^3 - 0.00021T -1.265t + 0.022T\text{x}t \qquad (10.1)$$

where:
SI = solubility index (ml insoluble/g dry solids)
M = moisture content (% w.b.)
T = storage temperature (^{o}C)
t = storage time (hour)

10.3.2. Effect of Moisture Content, Temperature and Time on Casein Colour

10.3.2.1. Experimental Results

Figure 10.6 shows the effect of storage temperature and moisture content on casein colour for a storage time of two hours (from the factorial and additional experiments described in Section 10.3.1.1). The results seem to indicate that only the samples held at 100^{o}C have a significant colour change resulting in the samples becoming more yellowish as moisture decreases. The effect of storage time and moisture content on colour of casein held at 100^{o}C is shown in Figure 10.7. The samples held for 2 hours had more severe discoloration than the other samples. Again the lower the moisture of the sample the more yellowish the colour.

The effect of the different factors on casein colour are quite difficult to assess based on visual appearance only. Hence the colour values of the samples were determined using the HunterLab Colorquest. The colour index of the samples were calculated using the ratio of the product of -L x b values to a-value. The summarized results of these analyses are shown in Appendix 10.5.

The plots for colour index against moisture content of samples from Figures 10.6 and 10.7 are shown in Figures 10.8 and 10.9. The colour index seems to describe the observations noted visually. The results show that the more severe the storage conditions the higher the colour index. The results also suggest that a difference of at least 300 colour index units is needed to have a significant visual colour change.

Sutermeister (1939) mentioned that casein dried at too high a temperature, or too long a time may become discolored. The lower the drying temperature that can be feasibly maintained the lighter in colour the end product will be. As drying temperatures

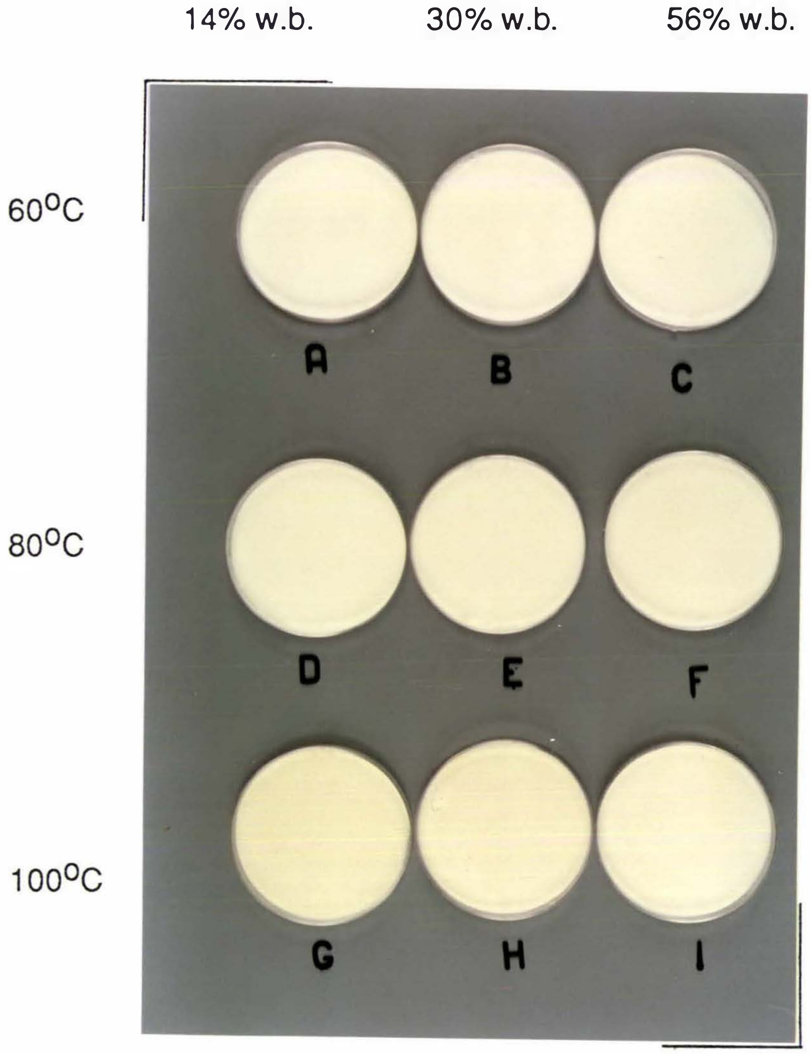


Figure 10.6. Effect of storage temperature and moisture content on colour of mineral acid casein held for 2 hours.

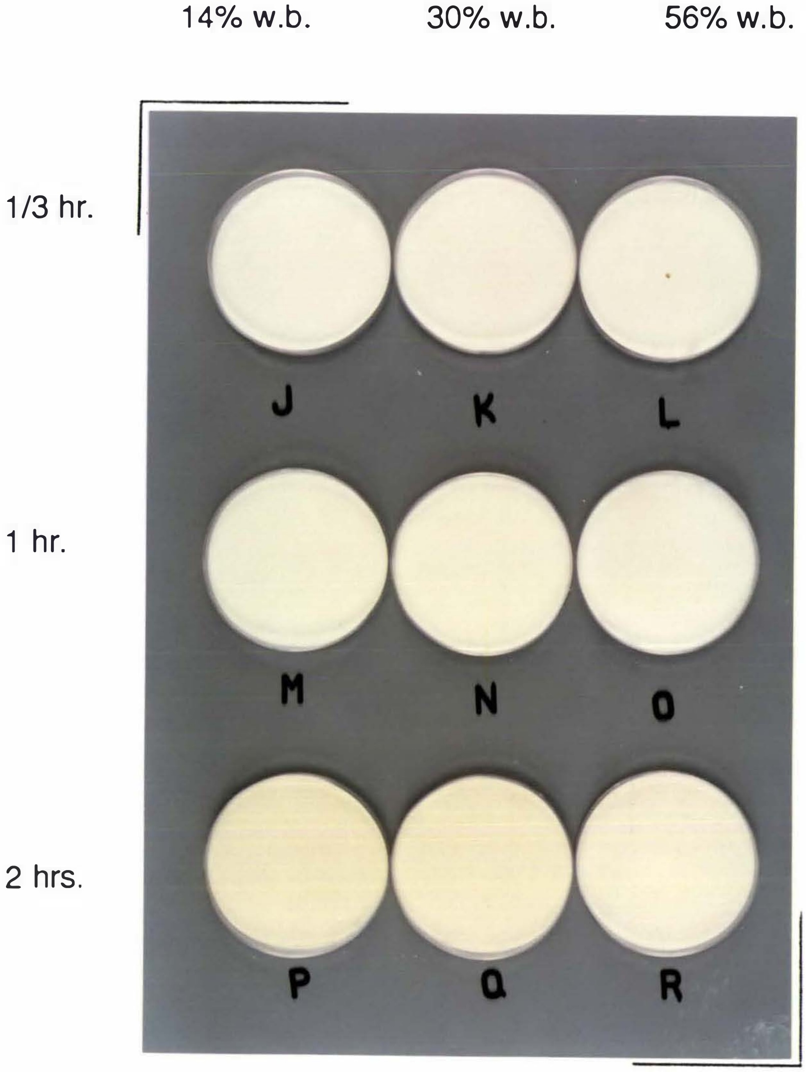


Figure 10.7. Effect of storage time and moisture content on colour of mineral acid casein held at $100^{o}C$.

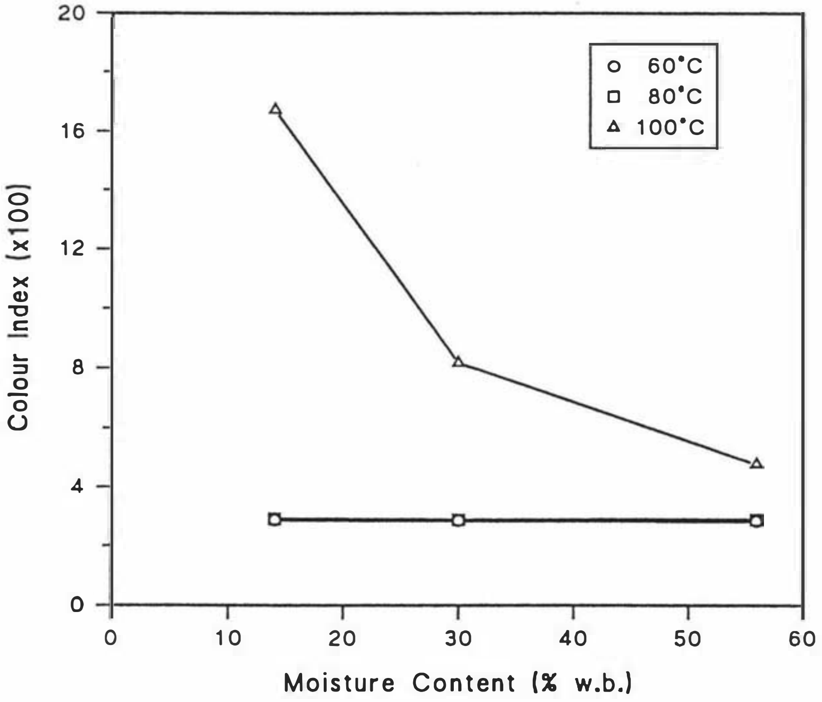


Figure 10.8. A plot of colour index against moisture content of mineral acid casein held at different temperatures for 2 hours.

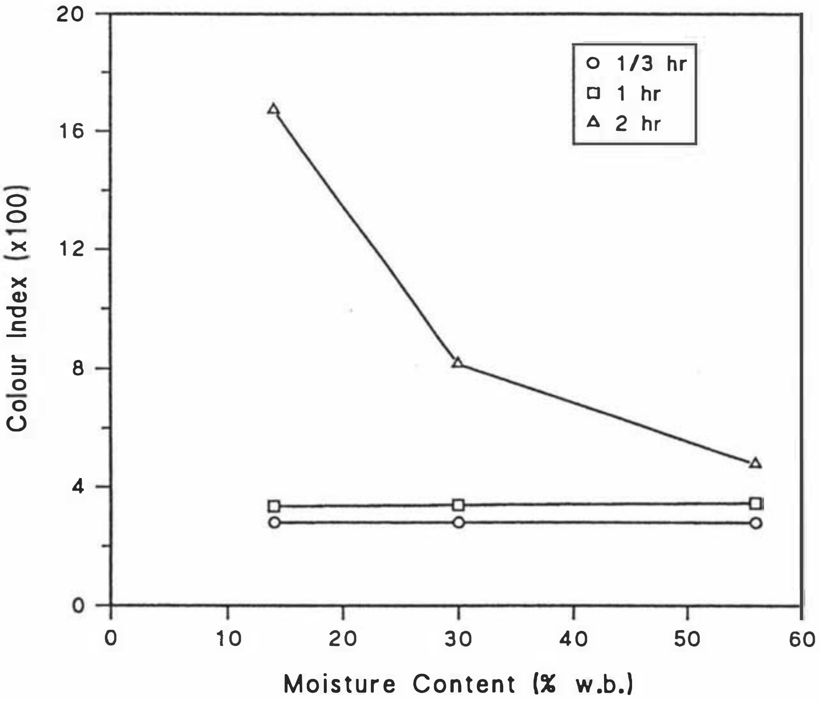


Figure 10.9. A plot of colour index against moisture content of mineral acid casein with different storage time held at 100°C.

increase above 55^{o}C, the curd will turn from white to ivory, yellow, orange and finally 'brick red' (the later denoting burnt casein) (Spellacy, 1953). Browning of casein during heating is an interaction between lactose and casein (Browne, 1939; Hall & Hedrick, 1966).

10.3.2.2. Multiple Regression Equation

Using the t-test procedure from Section 10.3.1.2, the important factors affecting the colour of casein were determined and summarized in Table 10.3. The top three factors/interactions affecting the colour of casein were the storage temperature, storage time and temperature-time interaction. In terms of the whiteness (L-value) of the samples, the effect of the three variables mentioned above were significant. For the greenness (a-value) of the samples, all the variables had a significant effect except for the moisture content-temperature interaction. The yellowness (b-value) of the samples are affected by all variables but the effect of moisture content was only significant at 95% level. However in terms of the colour index all variables were significant even at 99.9% level.

Multiple regression equations were fitted on the colour index only since it quantifies the observed colour of the samples into a single value. Using the same approach as in Section 10.3.1.2, several equations were derived. The first one was an equation that regressed the colour index in terms of the top three variables in linear form. The r^2 of this regression was only 45% which was very unsatisfactory. After manipulating the different variables by trial and error, the best equation found to describe the colour index of casein is in the form,

$$CI = 5925.10 - 142.65T + 0.87T^2 - 1409.50t + 336.06t^2 + 10.50T \times t \qquad (10.2)$$

where: CI = colour index

The r^2 of the above equation was only 61%. However the equation fitted the experimental data satisfactorily except for the three samples at 100^{o}C for 2 hours (Appendix 10.6). The equation predicts that these three samples would have very high colour indices indicating severe discoloration of the samples as observed in Figures 10.8 and 10.9 which is enough for descriptive purposes. The reason why the r^2 was low in spite of the good fit was due to the weighting effect of the regression towards the very high colour index. There were other equations which gave much higher r^2 but comparison of the predicted colour indices with the experimental data showed that the

Table 10.3. Summary of significant factors including interactions affecting the Hunter L-a-b colour values and colour index for mineral acid casein from the factorial experiments on wet and dry samples using the t-test procedure.

Factors and Interactions	Colour Values			Colour Index
	L	a	b	
Moisture Content (M)	0.08 ns	6.80 ***	3.28 *	28.47 ***
Temperature (T)	5.14 **	8.86 ***	14.15 ***	37.86 ***
Time (t)	5.39 **	10.91 ***	12.18 ***	38.19 ***
MxT Interaction	0.94 ns	2.24 ns	8.73 ***	28.43 ***
Mxt Interaction	0.27 ns	5.01 **	5.65 **	28.57 ***
Txt Interaction	5.64 **	10.82 ***	11.19 ***	37.48 ***
MxTxt Interaction	0.40 ns	4.20 **	6.17 **	28.33 ***

ns	not significant
*	significant at 95% level
**	significant at 99% level
***	significant at 99.9% level

above equation gave the best fit to the data.

10.4. THERMAL SENSITIVITY OF CASEIN

10.4.1. Casein Solubility

The moisture level with maximum solubility index can be predicted by differentiating Equation 10.1 from Section 10.3.1.2 with respect to moisture content,

$$0.000441M^2 - 0.038M + 0.772 = 0 \qquad (10.3)$$

The resulting equation is in quadratic form, hence using the quadratic equation to solve for the two roots,

$$M = 32.8\% \text{ w.b. or } 53.4\% \text{ w.b.}$$

Both roots result in positive values, but the smaller value would be the critical moisture content since the high moisture level will be in the constant rate period where no overheating of casein solids can occur. The value obtained was lower than the values quoted by Jebson (1991) for lactic casein.

Figure 10.10 shows a plot of solubility index against moisture content of three batches of mineral acid casein held at 100°C for one hour. The moisture content where the maximum solubility index occurred was around 30% (w.b.). The value was quite comparable with the predicted value using the regression equation and much lower than for lactic casein.

The moisture content of 30% (w.b.) or 43% (d.b.) is similar to the moisture content of casein at the end of the constant rate period for the laboratory fluidized bed drier (Section 6.3.1). At this point the casein solids temperature starts to increase above the wet bulb temperature of the drying air. However studies in Section 6.3.1 showed that the wet bulb temperature did not exceed 40°C for drying air temperatures of up to 132°C. This therefore suggests that insolubilization of casein is less likely to occur, as long as the inlet air temperature is not high enough to raise the wet bulb temperature to 60°C. However, extrapolation of Equation 10.1, suggests that significant insolubilization of casein at 60°C can occur even for a holding time of one minute.

Figure 7.3 indicates that for drying in a commercial NDA drier the most sensitive moisture content range of about 0.43 kg water/kg dry solids is well within the falling

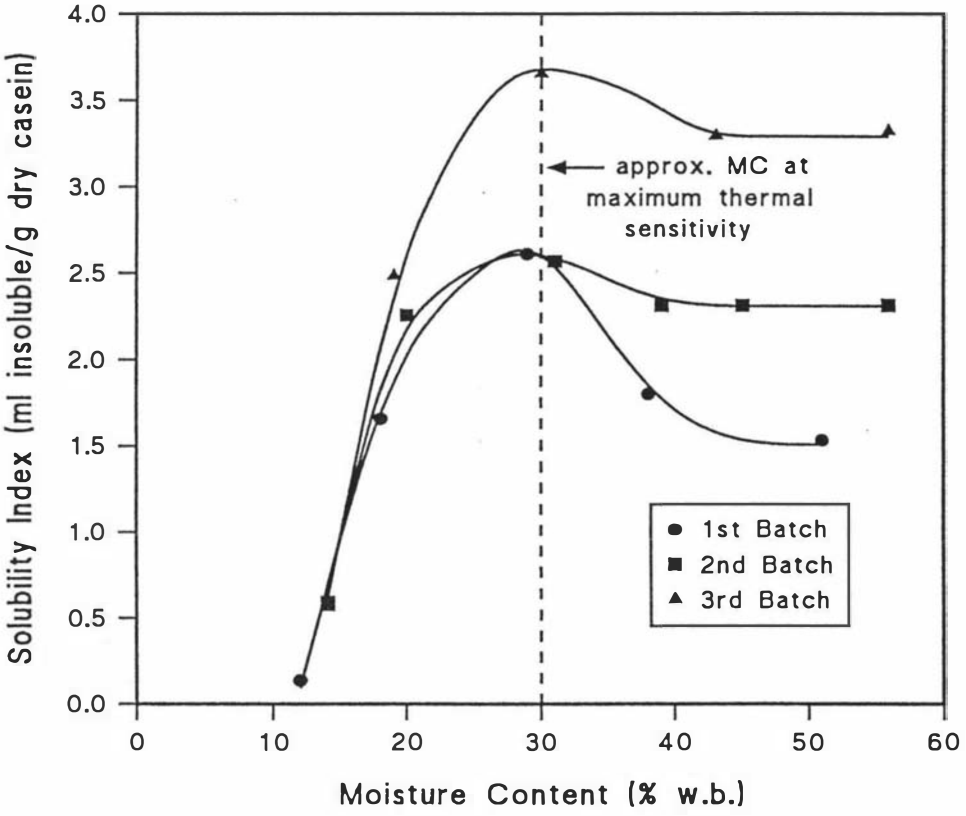


Figure 10.10. A plot of solubility index against moisture content of mineral acid casein held at 100°C for one hour.

rate period.

The overall conclusion is that casein driers should be designed to expose casein only to low temperatures during the most sensitive moisture content range at say 25-35% w.b. (0.33-0.54 kg water/kg dry solids).

10.4.2. Casein Colour

Equation 10.2 from Section 10.3.2.2 indicates that moisture content is not a significant factor affecting the colour of casein at temperatures below 100°C. At a temperature of 100°C and a short storage time (20 minutes), the moisture content also has no significant effect on the colour of casein. However when the storage time was increased to 2 hours there was an observable effect of moisture content on casein colour as shown by Figures 10.8 and 10.9. Also it was observed that there was some slight increase in the colour index with moisture content for samples held at 100°C for one hour. Hence the samples analysed for insolubles in Section 10.4.1 were also analysed critically for their colour using the HunterLab Colorquest.

However the variations of the lowest and the highest values for the three batches were less than 50 colour index units which is not very significant as pointed out in Section 10.3.2.1.

10.4.3. Thermal Sensitivity of Casein

The results show that at a moisture content of 30% (w.b.) the maximum solubility index of mineral acid casein occurs regardless of the storage temperature and time (within the experimental conditions used). At storage temperatures of up to 100°C and storage times of up to one hour at 100°C, the moisture content of the sample has no effect on the colour change. However when the storage time was increased to two hours at 100°C, there was severe discoloration of casein with a decrease in moisture content.

The results suggest that insolubilization and discoloration are important variables to consider for the thermal sensitivity of casein when drying at high inlet air temperatures. It is clear that the casein solids temperature should not reach 60°C since at this point it is very susceptible to insolubilization. Casein will have a significant colour change when exposed to high drying temperatures (solids temperature above 100°C) at all moisture levels if held for a long time (above 20 minutes). This may possibly happen in the falling rate period where casein temperatures increase with the air drying temperature, as curd gets held up and overdried.

10.5. EXPERIMENTS ON DRY CASEIN

10.5.1. Insolubility of Dry Casein During the Falling Rate Period

The previous studies have revealed that low moisture casein is sensitive to insolubilization if held above 100°C. During the falling rate period the temperature of casein solids approaches the air drying temperature. Hence the higher the air drying temperature the more likely that the drying casein would be insolubilized. A study was therefore conducted to determine the solubility index of casein at various times during the falling rate period.

Table 10.4 presents the solubility index of casein samples taken during the FRP at an air drying temperature of 136°C. The solubility index of casein increased during the FRP, but it was not clear whether this was due to moisture content, temperature, time or a combination of these factors. Between moisture contents of 0.02 and 0.08 kg water/kg dry solids a significant increase in solubility index occurred. A solubility index above 0.006 ml insoluble/g dry solids is considered to be a significant degree of insolubilization (Appendix 10.7).

10.5.2. Factorial Experiments

A factorial experiment was conducted on the effect of moisture content, temperature and time on the solubility index of dried casein. From the results in Table 10.4, the moisture content between 0.02 and 0.08 kg water/kg dry solids seemed to be the critical moisture for the increase in solubility index. Samples of 0.027 and 0.067 kg water/kg dry solids were used in the experiments. The sample with 0.067 kg water/kg dry solids was obtained by fluidized bed drying at 60°C and the 0.027 kg water/kg dry solids sample by vacuum drying (shelf temperature of 62°C) to further dry the casein. The use of low drying temperatures was to avoid any insolubilization of the casein beforehand. Two holding times (1/3 and one hour) and two storage temperatures (100 and 120°C) were used. A storage temperature of 100°C was used as the lowest temperature because it was around this temperature that significant insolubilization was observed (Table 10.4).

Table 10.5 summarizes the solubility index for the samples from the factorial experiments. Comparison of values with the maximum allowable solubility index shows that only the sample with 0.067 kg water/kg dry solids held at 120°C for

Table 10.4. Solubility index of commercial lactic casein taken during the falling rate period in a fluidized bed drier at an inlet air temperature of 136°C.

Residence time after the constant rate period (minutes)	Final Moisture Content (kg water/kg DS)	Outlet Temperature (°C)	Solubility Index (ml insoluble/ g dry casein)
3.5	0.13	41	0.003
5.5	0.08	58	0.003
7.5	0.04	86	0.005
11.5	0.02	110	0.012

Table 10.5. Solubility index for mineral acid casein from the factorial experiments on dry samples.

Sample Code	Moisture Content (% d.b.)	Storage Temp (°C)	Time (hour)	Test Moisture Content[c] (% d.b.)	Solubility Index[c] (ml insoluble/ g dry solids)
1	2.7	100	1/3	2.7	0.0015
2	6.7	100	1/3	6.7	0.0015
3	2.7	120	1/3	2.7	0.0020
4	6.7	120	1/3	6.7	0.0020
5	2.7	100	1	2.7	0.0020
6	6.7	100	1	6.7	0.0050
7	2.7	120	1	2.7	0.0050
8	6.7	120	1	6.7	0.0090
Control[d]	2.7, 6.7	---	---	2.7, 6.7	0.0010

c average of 2 replications

d dried samples not exposed to any storage temperatures hour was greater than this. The results indicate that no significant insolubilization of casein occured even after one hour at 100°C or for up to 20 minutes at 120°C.

Using the t-test procedure from Section 10.3.1.2, the significant factors including interactions were determined (Appendix 10.8). The results indicate that for dry casein the most critical factor affecting solubility index was the time (significant at 99.9% level of confidence). Temperature, moisture content, temperature-time interaction and moisture content-time interaction were still significant factors but only at 95% level of significance. The moisture content-temperature interaction and moisture content-temperature-time interaction were no longer significant variables affecting the solubility index of dry casein.

There was no significant colour change observed for all the samples.

CHAPTER 11
IMPLICATIONS OF THE RESULTS FOR CASEIN PROCESSING

11.1. IMPLICATIONS FOR WET PROCESSING

The processing steps from precipitation to dewatering of casein curd comprise the wet processing steps. Variations in the wet processing steps can affect the drying rates of casein curd. Possible critical variables were selected and their effects on the drying rates of casein curd were determined.

The precipitation temperature of casein had no significant effect on drying rates (Section 5.3.2). However the precipitation pH did influence the drying rates (Section 6.4.2). The lower the precipitation pH the higher the CRP drying rate and the higher the FRP drying rate. Overall the results suggest that high pH curd takes longer to dry.

The hot wash temperature for casein curd had no influence on the drying rates (Section 5.3.3).

Dewatering conditions clearly influence drying rates. In a decanter centrifuge when the dewatering temperature is sufficiently high plasticization of curd may occur (Munro *et al*., 1983). In the CRP, semi plasticized curd had a similar drying rate to the standard curd but severely plasticized curd had a low drying rate. Both semi and severely plasticized samples had higher drying rates in the FRP than standard casein curd (Section 6.4.3). This was surprising but probably resulted because plasticization gave the casein particle more rigidity, reducing shrinkage and delaying surface sealing. Increasing the dewatering temperature decreased the CRP drying rate of casein curd but the effect on the FRP drying rate depended on the curd pH. Below pH 4.6, increasing the dewatering temperature increased the FRP drying rate but above pH 4.6 the trend was reversed. These results indicate that dewatering conditions need to be properly controlled in order to maintain the same curd characteristics during drying.

In conclusion, it is important to control the wet processing steps, particularly precipitation pH and dewatering temperature, so that the drying characteristics of casein curd remain as consistent as possible.

11.2. IMPLICATIONS FOR DRYING

11.2.1. Overview of the Changes in Casein Particles During Drying

Drying casein from 1.2 kg water/kg DS to a final MC of 0.02 kg water/kg DS caused particle shrinkage of about 40% (Section 8.3.1). The shrinkage of particles was caused by evaporation of water and contraction of the casein matrix. When moisture content fell below 0.40 kg water/kg DS, the casein matrix no longer contracted as easily to fill the space left behind by the evaporating moisture and the space become air pores (Section 8.3.2). Lactic casein particles contained more air pores than mineral acid or rennet casein particles (Section 8.3.1) and therefore tended to have higher drying rates in the FRP (Section 6.4.4).

The self diffusion coefficient (D) of water in caseins reflects the molecular mobility of the unbound water. The excess moisture above 0.30 kg water/kg DS is unbound or free, while below this moisture level virtually all the water is bound (Section 9.3). The three types of casein had similar D values above the unbound moisture range (Section 9.3) and as a consequence there was no significant difference in their CRP drying rates (Section 6.4.4). Below 0.30 kg water/kg DS moisture content, the water behaved differently from bulk water so that more than the latent heat of vaporization of pure water was needed to evaporate the remaining moisture in casein particles (Section 4.3). Mineral acid casein had a higher heat of desorption than rennet and lactic caseins in the bound moisture range (Section 4.3), and this corresponded to a lower FRP drying rate for mineral acid casein (Section 6.4.4).

11.2.2. Summary of Data Relevant to Drier Design and Control

The equilibrium moisture content (EMC) data for the three types of casein (Section 4.1) provide information for the moisture content driving force during the FRP, and enable estimation of the final moisture content achievable under various drying conditions.

Air inlet temperature and air velocity are the main variables that can be controlled in a drier. Increasing the air inlet temperature increased the drying rates of casein in both the CRP and FRP. The evaporation rate in the CRP was directly proportional to the temperature driving force, while the FRP drying coefficient increased exponentially with drying temperature (Section 6.3.1). The CRP drying rate of casein increased with air velocity, but air velocity had no effect on the drying rate in the FRP (Section 6.3.2). The results suggest that air inlet temperature control is important in both CRP and FRP since it influences the drying rates significantly. Air velocity control is only important in the CRP, and its use is also limited by the fluidization characteristics of the casein curd.

It was observed that the stickiness of casein was a problem at high casein moisture, at high air inlet temperatures and at low airflow conditions. However, when the curd was introduced to the drier at ambient temperature and the temperature then increased to the required level (up to 132°C), stickiness of the curd was much less of a problem under the same airflow conditions because the casein had partly dried, improving fluidization characteristics (Sections 6.1.2 and 6.3.1). This suggests that in drying wet curd, good fluidization must be maintained to avoid particle clumping and lower drying temperatures at the curd inlet would also reduce stickiness.

The CRP drying rate decreased for casein particles larger than 2.00 mm because of reduced fluidization efficiency. However, the casein particle size had no effect on the drying rate in the FRP for the size range between 0.50 and 3.35 mm. Furthermore casein particles must be size reduced in order to avoid wide moisture differences within (Section 9.6.2) and between particles (Section 7.2.1).

Insolubilization and discoloration are important variables for monitoring thermal damage to casein during drying at high air inlet temperatures (Chapter 10). Casein was most sensitive to thermal damage at a moisture content of about 30% (w.b.) (0.43 kg water/kg DS). At this moisture content significant insolubilization occurred when the casein solids reached 60°C or higher even for a short time (Section 10.4). During the FRP, the temperature of casein solids approaches the air inlet temperature. However for solids temperatures as high as 120°C during the FRP, no significant insolubilization of dry casein occurred as long as the residence time was short (< 20 minutes) (Section 10.5.2).

The adsorption of moisture for mineral acid casein was affected by the drying method used. The more severe the drying conditions the lower the moisture adsorption (Section 4.4). This change in equilibrium moisture adsorption reflects a change in the physical state of the protein which is likely to lead to some functionality changes in the product.

11.3. IMPLICATIONS FOR DRIER DESIGN AND CONTROL

11.3.1. Drier Design

A proposed new design concept for casein dry processing is shown in Figure 11.1. The design consists of three major items namely: a) a predrier; b) a final drier; and c) a

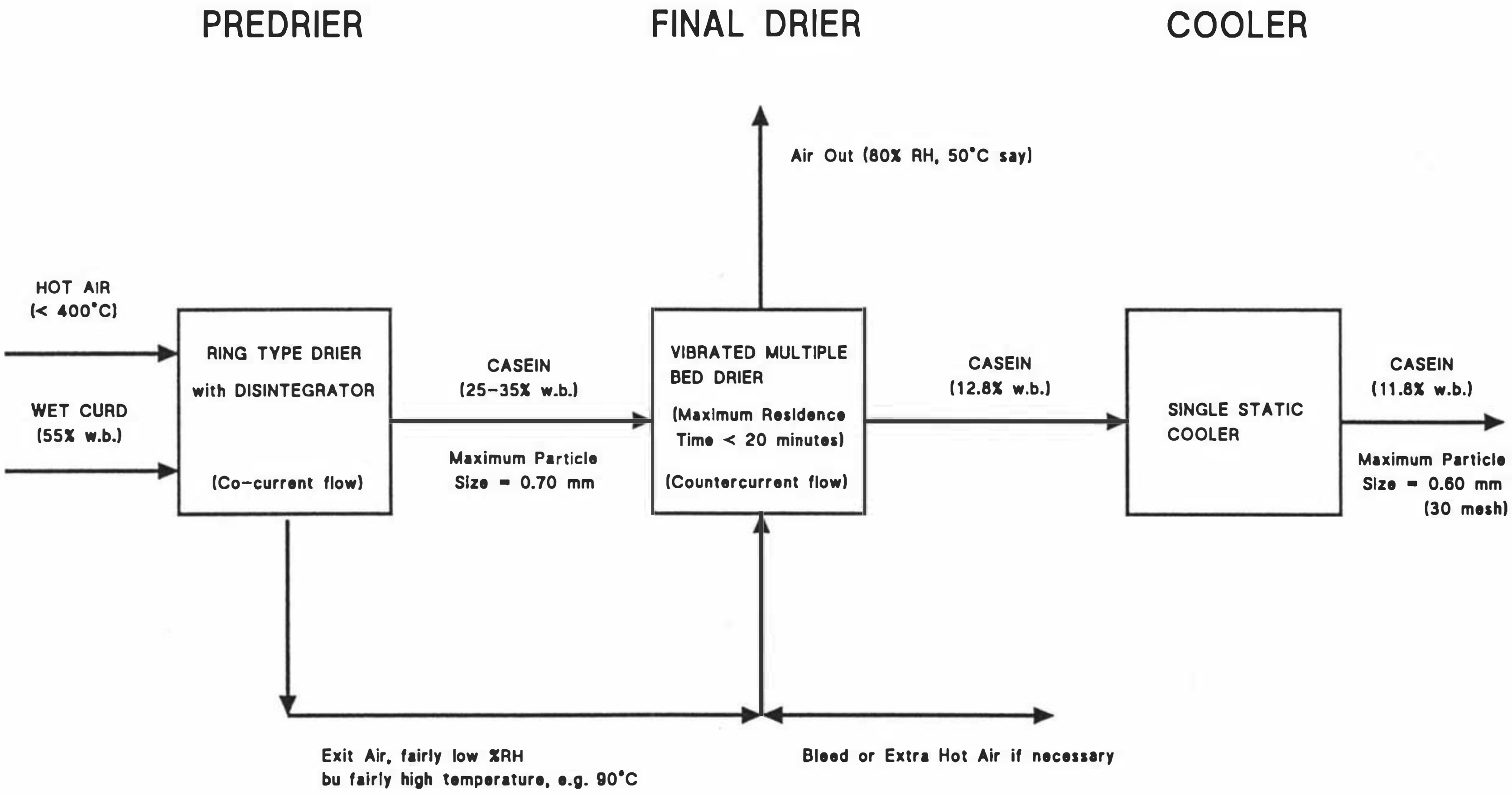


Figure 11.1. Possible new design concept for casein dry processing.

cooler. The critical points for the whole process are:

a) the maximum temperature in the predrier;
b) the maximum particle size out of the predrier;
c) the moisture content range for transfer of casein from the predrier to the final drier; and
d) the maximum residence time in the final drier.

Only a short residence time is needed in the predrier because of the fast initial drying rate but the final drier will require a long residence time for the slower drying in the falling rate period. The cooler will reduce the temperature of the dried casein before discharge to the next processing step.

The drying of the curd in the predrier should be designed to occur in the constant rate period. Hence the use of high airflows and temperatures in the predrier should evaporate the moisture from the curd rapidly.

The casein should be discharged from the predrier with a maximum particle size about 10% bigger (Section 8.3.1) than 30 mesh (0.6 mm) to give allowance for shrinkage until reaching the end of the cooler. The temperature, airflow, disintegrator speed and classifier settings would need to be adjusted to avoid producing too fine a casein particle. This should not be a problem as the residence time will be less than in current commercial ring driers.

Thermal damage to the casein is minimized in the sensitive intermediate moisture range by using cocurrent flow above this moisture range in the ring drier and countercurrent flow below it in the vibrated bed drier. By using cocurrent flow initially, the wet casein curd is contacted with the highest temperature air while at the end of the drier lower temperature air is contacting the partly dried casein as it approaches the thermally sensitive moisture level. There is no risk of overheating the wet curd in the initial stage of drying since it is still in the CRP and the temperature will not rise above the wet bulb temperature of the air (Section 6.2.1). In the second drying stage countercurrent flow is used so that the driest casein is in contact with the highest temperature air while the moist casein near the thermally sensitive moisture is in contact with lower temperature air. The dry casein is not sensitive to insolubilization in the FRP for solids temperature up to 120^{O}C as long as the residence time is less than 20 minutes (Section 10.5.2).

The use of countercurrent flow in the final drier should also assist drying rates. The driest casein is exposed to the highest temperature and lowest relative humidity air

(Section 6.3.1), both of which will increase moisture diffusion rates.

Particle clumping during the early drying stages as a consequence of curd stickiness (Section 6.1.2) should not be a problem because of the use of high airflows and the disintegrator in the predrier.

The overall rationale of the design is to reduce particle size during drying to minimize the need for tempering and grinding and to allow better control of casein moisture content leaving the drier (Section 7.2.1). The need for tempering is reduced by using a small particle size and a long bed residence time in the final drier and cooler. The need for post-drier grinding is also reduced because of the disintegrator in the predrier.

Energy efficiency of the system should be high with the proposed air flow pattern and temperatures.

11.3.2. Drier Control

The drying characteristics of casein curd are affected by the wet processing steps (Section 11.1). It is therefore important that there is good control of the wet processing steps, particularly precipitation pH and dewatering temperature in order to simplify drier control.

Air flowrate and air inlet temperature are two variables which clearly have potential for use in drier control. Increasing either air velocity or air inlet temperature results in an increase in drying rate. Changes in air velocity change the fluidization conditions in the bed so only a small range of air velocities can be used in practice. An upper limit is set on air inlet temperature by the need to minimize the thermal damage to the casein, and this limit will depend on the drier configuration.

The humidity driving force may be an alternative control parameter. The use of humidity probes for drier control is clearly not yet straightforward because of the poor response time and unreliability of these devices under the prevailing conditions in the drier (Section 6.1.4). However these probes should be useful under ambient conditions, e.g. humidity compensation. The poor response time will not be a concern in continuous driers since changes in drying air will be less rapid.

11.4. IMPLICATIONS FOR POST-DRIER PROCESSING AND STORAGE

The moisture content of large casein particles was significantly higher than smaller particles at the drier exit (Section 7.2.1). It is therefore helpful to reduce the particle size to minimize wide moisture variation between particles. The time for moisture equilibration between different size particles was about 3 hours (Sections 7.2.2 and 9.5). This indicates that the tempering of casein could be achieved in less than the 24 hour period currently used, provided no very large particles need to be tempered. (It is also possible that some mechanical change occurs during tempering in addition to moisture equilibration).

CHAPTER 12

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LEMUEL M. DIAMANTE, PETER A. MUNRO and MICHAEL G. WEEKS. Moisture desorption isotherms and drying rates of mineral acid casein. **Proceedings of the CHEMECA 1990** (Australasian Chemical Engineers Conference on 27-30 August 1990, Auckland, New Zealand). Volume 2. pp. 101-108.

MORISON, K.R., COLLINS, S., PEARCE, V. & OLIVER, R. (1990). Moisture loss from dry lactic acid casein during air conveying. **Report No. ES90R16. New Zealand Dairy Research Institute, Palmerston North**. (Desorption isotherm data used in the calculations of the humidity driving force for moisture loss)

BACK, P.J., COY, A., XIA, Y, CALLAGHAN, P.T., DIAMANTE, L.M. & UMBACH, S.L. (1991). Some biophysical applications of motional contrast in n.m.r. microscopy. **International Journal of Biological Macromolecules. 13**: 181-189.

LEMUEL M. DIAMANTE, PETER A. MUNRO and MICHAEL G. WEEKS. Moisture desorption isotherms of three types of casein at a temperature range between 25 and 80°C. **Journal of Dairy Research** (Submitted to the Editor).

More papers will be written after submission of the thesis.

CHAPTER 13
APPENDICES

APPENDIX 2.1
Shrinkage in dehydration of root vegetables

Data from Figure 2 of Suzuki *et al.* (1976),

Sample	Moisture Content (kg water/kg dry solids) M_o	M	Original Surface Area, A_o (cm^2)	A/A_o
Potato 1	4.42	0.442	7.63	0.415
2	4.21	0.421	7.39	0.485
3	4.88	0.976	8.00	0.635
Sweet Potato 1	3.02	0.604	7.80	0.655
2	3.26	0.326	7.50	0.545
3	3.29	0.329	8.35	0.265

Using the mean values for potato: M_o=4.503 kg water/kg DS; M=0.613 kg water/kg DS; A_o=7.673 cm^2 and A/A_o=0.512,

$$A = (0.512)(7.673\ cm^2) = 3.929\ cm^2$$

$$d = \sqrt{((4)(3.929))/\pi} = 2.237\ cm$$

$$A_o = 7.673\ cm^2,\ d_o = 3.126\ cm$$

Therefore,

$$V = ((\pi)(2.237)^3)/6 = 5.861\ cm^3$$

$$V_o = ((\pi)(3.126)^3)/6 = 15.994\ cm^3$$

$$V/V_o = 5.861/15.994 = 0.366$$

APPENDIX 3.1

Calculations for Determining the Moisture Content at a Given Time for the Tunnel Drying Data

1. The average moisture content (kg water/kg dry solids) of casein at the end of drying (M_f) was determined by getting a representative sample from the drying tray.

2. Using the value of M_f and the mass of casein at the end of drying period (W_f), the mass of dry solids on the samples (W_{ds}) was determined using the equation,

$$W_{ds} = \frac{W_f}{M_f + 1} \qquad \text{(A3.1)}$$

3. Using the calculated value of W_{ds}, the moisture content of the sample at any time (t) can be computed using the equation,

$$M_t = \frac{W_t - W_{ds}}{W_{ds}} \qquad \text{(A3.2)}$$

Sample Calculations:

Given:

M_f = 0.0595 kg water/kg dry solids

W_f = 0.1083 kg

Solving for W_{ds} using equation (A3.1),

$$W_{ds} = \frac{(0.1083 \text{ kg})}{0.0595 + 1} = 0.1022 \text{ kg}$$

Solving for M_t at any given time using equation (A3.2), at t=15 minutes, W_{15} = 0.2983 kg,

$$M_{15} = \frac{(0.2983 - 0.1022) \text{ kg}}{0.1022 \text{ kg}} = 1.9188 \text{ kg water/kg dry solids}$$

APPENDIX 3.2
Calculations for the Percentage Volume of Casein, Water and Air Components

Sample: Pilot Plant Lactic Casein (before drying)

Water Free Density of Lactic Casein, ρ_c = 1.363 g/cm^3

Density of Water at 30°C, ρ_w = 0.996 g/cm^3

Mass of Particle, W_p = 1.7907 g

Volume of Particle, V_p = 3.43 cm^3

Moisture Content of Particle, M_p = 1.1761 kg water/kg dry solids (g/g)

Assumption:

The mass, density and hence volume of casein does not change over the drying process.

CALCULATIONS:

Solving for the mass (W_c) and volume (V_c) of dry casein,

$$W_c = \frac{W_p}{1 + M_p}$$

$$= \frac{1.7907\text{g}}{1 + 1.1761\ \text{g/g}}$$

$$W_c = 0.8229\ \text{g}$$

$$V_c = \frac{W_c}{\rho_c}$$

$$= \frac{0.8229\text{g}}{1.363\ \text{g/cm}^3}$$

$$V_c = 0.60\ \text{cm}^3$$

Solving for the mass (W_w) and volume (V_w) of water,

$$W_w = W_p - W_c = 1.7907 - 0.8229 = 0.9678 \text{ g}$$

$$V_w = \frac{0.9678\text{g}}{0.996 \text{ g/cm}^3}$$

$$V_w = 0.97 \text{ cm}^3$$

Solving for the volume of air (V_a),

$$V_a = V_p - V_c - V_w = 3.43 - 0.60 - 0.97 = 1.86 \text{ cm}^3$$

Solving for the percentage volume of components,

$$\text{\% Volume of casein} = \frac{0.60\ (100)}{3.43} = 17.6\%$$

$$\text{\% Volume of water} = \frac{0.97\ (100)}{3.43} = 28.3\%$$

$$\text{\% Volume of air} = \frac{1.86\ (100)}{3.43} = 54.2\%$$

APPENDIX 3.3
Procedure for the Solubility Tests on Acid Casein

Weigh 10 g casein into a 250 ml beaker.

Add 78 ml distilled water.

Stir with a glass rod to evenly wet the casein. (Try not to spread the casein around the beaker above the water line.)

Place the beaker containing the casein and water into a 60.0($\pm$0.5^{o}C) water bath and start stirring using a mechanical stirrer (Heidolph Type RZR 50, Germany) set at 300 rpm.

Add 12 ml of 0.5 N NaOH. (Prepared by dissolving 20.40 g of 98% pure NaOH to 1 litre of distilled water.)

After 60 minutes of stirring, remove beaker from the water bath and pour 37 ml of the solution into a centrifuge tube. (Ensure it is a representative sample i.e. well mixed.)

Centrifuge in an automatic centrifuge (Sorvall SS-3, Du Pont Instruments, USA) for 10 minutes at 2000 rpm.

Pour off the supernatant and transfer the insoluble matter to a 10 ml centrifuge tube (with the narrow tip and 0.01 ml graduations) with the aid of a thin metal rod and a few mls of water from a squeeze water bottle.

Centrifuge for 5 minutes at 2000 rpm.

Read the volume of the sediment material in the centrifuge tube as soon as the centrifuging has finished.

Measure the pH of the final solution. If it is outside 6.7 and 7.0 repeat the analysis.

APPENDIX 4.1

Sample printout for the BET regression of the isotherm for mineral acid casein at 53°C

```
aw/[Mm(1-aw)]          aw
     Y                 X
     2.394           0.110
     2.603           0.110
     2.679           0.110
     3.137           0.206
     3.270           0.206
     3.140           0.206
     4.352           0.299
     4.537           0.299
     4.623           0.299
     6.881           0.440
     6.826           0.440
     7.021           0.440

plot of Y versus X

        8  +
           :
           :                                            *
           :                                            2
           :
        6  +
           :
           :
    Y      :                          *
           :                          2
        4  +
           :
           :                3
           :    2
           :    *
        2  +
            +---------+---------+---------+---------+---------+
         0.080     0.160     0.240     0.320     0.400     0.480
                                    X
```

```
 The regression equation is :

 Y = 0.732 + 13.484 X

Column              Coeff          SD(Coeff)         t-value
 constant            0.732           0.236             3.11
 X                  13.484           0.811            16.62

the residual standard deviation about the model is S = 0.342
with 11 - 1 = 10 degrees of freedom

R-squared =  96.51%

Analysis of Variance
Due to                    SS        DF          MS=SS/DF
Regression             32.337        1          32.337
Residual                1.171       10           0.117
Total                  33.507       11
```

APPENDIX 4.2

Sample calculations for the M_m and C parameters of the BET equation for mineral acid casein 53^{o}C

The two-constant BET equation is,

$$\frac{a_w}{M_e(1-a_w)} = \frac{1}{M_mC} + \frac{(C-1)}{M_mC} a_w$$

Let $Y = a_w/[M_e(1-a_w)]$ and $X = a_w$, hence the intercept $(I) = 1/(M_mC)$ and

the slope $(S) = (C-1)/(M_mC)$.

Also,

$$M_mC = 1/I \quad ; \quad M_mC = (C-1)/S$$

Therefore,

$$C = \frac{S}{I} + 1 \quad \text{and} \quad M_m = \frac{1}{I\ C}$$

Using the data from Appendix 4.1 for mineral acid casein at 53^{o}C,

$$C = \frac{13.48}{0.732} + 1 = 19.4$$

and,

$$M_m = \frac{1}{(0.732)(19.4)} = 0.0704 \text{ kg water/kg dry solids}$$

APPENDIX 5.1

Sample calculations for solving the CRP drying rate of casein curd using the heat transfer approach

Considering the first sample (whey pH=4.62),

Air temperature, $T_a = 80^oC$

Wet bulb temperature, $T_w = 31^oC$

Air velocity, V = 5.0 m/s

Weight of dry solids, W_s =0.1024 kg

Drying surface area, A = assumed to be equal to the area of the tray exposed to the drying air
= exposed area of the top + exposed area of the bottom + two exposed sides parallel to the flow
= (0.167 m)(0.167 m) + (0.134 m)(0.168 m) + 2(0.035 m)(0.167)
= 0.0621 m^2

Density of the air at T_a, ρ_a = 1.014 kg/m^3 (from Singh & Heldman, 1984)

Latent heat of vaporization at T_w, $\lambda = 2.558 \times 10^3$ kJ/kg water (from Singh & Heldman, 1984)

Calculations:

Solving for the heat transfer coefficient (h) for parallel air flow,

$$h = 14.3\ G^{0.8} \qquad \text{where: } G = \rho_a\ V$$

$$h = 14.3\ (\rho_a\ V)^{0.8}$$

$$= 14.3\ ((1.014)(5.0))^{0.8}$$

$$= 52.401\ W/m^{2o}C$$

Solving for the CRP drying rate $(dM/dt)_c$,

$$(dM/dt)_c = \frac{h\ A\ (T_a - T_w)}{W_s\ \lambda}$$

$$= \frac{(52.401)(0.0621)(80 - 31)}{(0.1024)(2558000)}$$

$$(dM/dt)_c = 6.087 \times 10^{-4} \text{ kg water/kg DS*sec}$$

APPENDIX 5.2

Sample calculations for solving the EMC of casein curd using the desorption isotherm equation

From section 4.1.2, the desorption isotherm equation for laboratory mineral acid casein curd at 80°C is,

$$\ln M_e = 2.361 + 0.429 (\ln(-\ln(1-a_w))$$

where: M_e = equilibrium moisture content, EMC (% dry basis)

a_w = water activity = ERH/100

ERH = equilibrium relative humidity

Calculation:

Solving for the EMC of the first sample (whey pH=4.62); ERH=2.8%; a_w=0.028,

$$\ln M_e = 2.361 + 0.429 (\ln(-\ln(1 - 0.028))$$

$$= 2.361 + 0.429 (-3.56138)$$

$$\ln M_e = 0.833166$$

therefore,

$$M_e = 2.30\% \text{ dry basis} = 0.023 \text{ kg water/kg dry solids}$$

APPENDIX 5.3

Effect of precipitation temperature on drying rate curve parameters of laboratory made mineral acid casein curd

Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Precipitation Temp. (°C)	CRP drying Rate ($\times 10^{-4}$ kg water/ kg DS*sec)	FRP Drying Coefficient ($\times 10^{-4}$ sec^{-1})		Critical MC (kg water/kg DS)		Final Apparent EMC (kg water/kg DS)
		First	Second	First	Second	
35	6.81	3.26	6.23	1.49	0.75	0.01
45	6.54	2.81	6.15	1.55	0.73	0.03
53	6.03	3.93	5.07	1.50	0.42	0.04
60	7.15	3.49	6.39	1.54	0.66	0.04
Mean with 95% confidence interval						
	6.6±0.8	3.4±0.7	6.0±1.0	1.52±0.05	0.64±0.24	0.03±0.02

APPENDIX 5.4

Effect of hot wash temperature on drying rate curve parameters of laboratory made mineral acid casein curd

Drying conditions: tunnel drier, DBT=80°C, air velocity=5 m/s, ambient humidity.

Hot Wash Temperature (°C)	CRP drying Rate ($\times10^{-4}$ kg water/kg DS*sec)	FRP Drying Coefficient ($\times10^{-4}$ sec^{-1})		Critical MC (kg water/kg DS)		Final Apparent EMC (kg water/kg DS)
		First	Second	First	Second	
55	5.52	2.16	4.88	1.60	0.83	0.06
75	6.03	3.93	5.07	1.50	0.42	0.04
95	5.79	3.21	4.16	1.59	0.84	0.04
Mean with 95% confidence interval						
	5.8 ± 0.6	3.1 ± 2.2	4.7 ± 1.2	1.56 ± 0.14	0.70 ± 0.60	0.05 ± 0.03

Appendix 6.1
Sample Calculations for the Data Plotted in Figure 6.9

Sample: Commercial Lactic Casein Temperature: 81 C

AVAILABLE DATA:

Weight of dry solids, Ws = 2.4 kg DS
CRP dM/dt = .0006677 kg water/(kg DS*sec)
CRP time, tc = 936 seconds
Initial MC, M1 = 1.005 kg water/kg DS
Initial Humidity, W1 = .0082 kg water/kg DA
MC at end of CRP, M2 = .38 kg water/kg DS
Inlet temp. of Drying air, Ta1 = 81 C
Wet bulb temp. of drying air, Twb = 31
During CRP the casein solids temperature (Tc1 & Tc2) are constant and approximately equal to Twb
Pressure Drop thru the orifice, P = 80 mm water
Latent Heat of Vaporization, HL = 2257 kJ/kg water
Specif. Heat of Casein Solids, Cpc = 1.54 kJ/kg DS*C
Heat loss from the drier, Q = .019 kW or kJ/sec
Latent Heat of Evap. of Water at Twb, λ = 2429000 J/kg water

CALCULATIONS:

Solving for the mass flowrates of air (ma) and casein solids (mc),

ma = 0.009805(P)^1/2 = .0876986 kg DA/sec

mc = Ws/tc = .0025641 kg DS/sec

Solving for the outlet humidity of drying air (W2),

W2 = (ma*W1 + mc*M1 - mc*M2)/ma

W2 = .0264735 kg water/kg DA

Solving for the humid heat for inlet (Cs1) and outlet (Cs2) air,

Cs1 = 1.005 + 1.88*W1 = 1.020416 kJ/kg DA*C

Cs2 = 1.005 + 1.88*W2 = 1.05477 kJ/kg DA*C

Solving for the enthalpy for inlet (Ha1) and outlet (Ha2) air,

Ha1 = Cs1*Ta1 + W1*HL = 101.1611 kJ/kg DA

Ha2 = Cs2*Ta2 + W2*HL = 1.05477 Ta2 + 59.75079 kJ/kg DA

Solving for enthalpy for inlet (Hc1) and outlet (Hc2) casein solids,

Hc1 = Cpc*Tc1 + 4.175*M1*Tc1 = 177.8121 kJ/kg DS

Hc2 = Cpc*Tc2 + 4.175*M2*Tc2 = 96.9215 kJ/kg DS

Solving for the outlet temp. (Ta2) of the drying air,

Ha2 = (ma*Ha1 + mc*Hc1 - mc*Hc2 - Q)/ma

1.05477 Ta2 + 59.75079 = 103.3095

Ta2 = 41.29687°C

Solving for the log mean temp. difference ((Ta-Twb)lm),

(Ta-Twb)lm = ((Ta1-Twb) - (Ta2-Twb))/(ln ((Ta1-Twb)/(Ta2-Twb)))

(Ta-Twb)lm = 25.12565°C

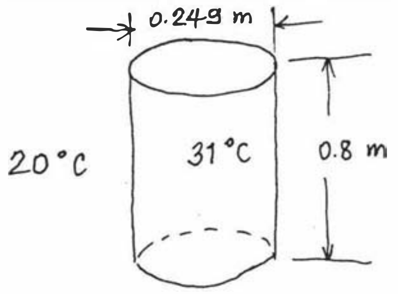
Solving for the product of drying surface area (A) & CRP drying rate (Rc),

ARc = dM/dt*Ws = .0016025 kg water/sec

Solving for the ratio of the LMTD and latent heat of evaporation,

(Ta-Twb)lm/ λ = .0000103°C kg/J

CALCULATIONS FOR HEAT LOSS



ΔT = 11°C

L = 0.8 m

Tf = (31 + 20)/2 = 25.5 C say 25 C

from Ranznevic (1978),

ρ = 1.1455 kg/m^3
β = 3.355x10^-3 K
Cp = 1.0125 kJ/kg K
k = 0.02545 W/m K
μ = 18.461x10^-6 Pa.s
Pr = 0.71
g = 9.81 m/s^2

Solving for Gr,

Gr = (L^3 ρ^2 g β /\T)/μ^2 = 7.14E+08

also, Gr.Pr = 5.07E+08

since 10^4 < Gr.Pr < 10^9; a = 0.59 & m = 1/4

also,

Nu = (h L)/k = a (Gr.Pr)^m

therefore, h = 2.82 W/m^2 K

Solving for the convective heat loss,

A = π D L = 0.626 m^2

Q = h A ΔT = 19 W = 0.019kW

Appendix 6.2

Calculations for the 'Apparent Activation Energy' of Casein

The 'apparent activation energy' for drying in the falling rate period can be calculated from the Arrhenius equation,

$$S = \frac{-E_a}{R}$$

where: S = the slope of the regression for the plot of ln F against 1/T

E_a = activation energy

R = gas constant (8.314 J/mole^{o}K)

From Figure 6.10, S = -2132.3, hence solving for the 'apparent activation energy' of casein,

$$E_a = (2132.3)(8.314) = 17727 \text{ J/mole} = 17.73 \text{ kJ/mole}$$

Appendix 6.3
Sample Calculations for the Drying Times of Casein Curd

Considering the data on mineral acid casein curd dewatered in the Conturbex from Table 6.9 and using the following equations,

$$t_c = \frac{(M_i - M_c)}{R}$$

$$t_f = \frac{\ln \left| \dfrac{M_c - M_e}{M_f - M_e} \right|}{F}$$

$$t_t = t_c + t_f$$

where: t_c = drying time in the CRP
M_i = initial moisture content
M_c = critical moisture content
R = CRP drying rate
t_f = drying time in the FRP
M_e = equilibrium moisture content
M_f = final moisture content
(based on 12% w.b. or 0.136 kg water/kg DS)
F = FRP drying coefficient
t_t = overall drying time

$$t_c = \frac{(1.34 - 0.47)}{0.000802} = 1084.8 \text{ s} = 18.08 \text{ minutes}$$

$$t_f = \frac{\ln \left| \dfrac{0.47 - 0.057}{0.136 - 0.057} \right|}{0.00193} = 857.0 \text{ s} = 14.28 \text{ minutes}$$

$$t_t = 18.08 + 14.28 = 32.36 \text{ minutes}$$

Appendix 6.4

Calculations for the Uncertainties at 95% Confidence on Drying Times for Mineral Acid Casein Curd Dewatered in the Conturbex

Using the same data as in Appendix 6.3.

Solving for the drying time in CRP and the 95% confidence bound,

$$t_c = \frac{(1.34 \pm 0.10) - (0.47 \pm 0.03)}{0.000802 \pm 0.000024} \qquad Br1 = \sqrt{0.10^2 + 0.03^2} = 0.1044$$

$$= \frac{0.87 \pm 0.104}{0.000802 \pm 0.000024} \qquad F1 = \frac{0.104}{0.87} = 0.1195$$

$$F2 = \frac{0.000024}{0.000802} = 0.0299$$

$$Z = \frac{0.87}{0.000802} = 1084.8 \text{ s} \qquad Fr = \sqrt{0.1195^2 + 0.0299^2}$$

$$= 0.123$$

$$Br2 = (1084.8)(0.123) = 133.7 \text{ s}$$

Hence,

$$t_c = Z \pm Br2$$

$$= 1084.7 \pm 133.7 \text{ seconds}$$

$$= 18.08 \pm 2.23 \text{ minutes}$$

Solving for the time in the FRP and the 95% confidence bound,

$$t_f = \frac{\ln\left[(M_c - M_e)/(M_f - M_e)\right]}{F}$$

$$= \frac{\ln \left| \dfrac{0.47 \pm 0.03 - 0.057 \pm 0.010}{0.136 \pm 0.02 - 0.057 \pm 0.010} \right|}{0.00193 \pm 0.00005} \qquad \begin{aligned} Br1 &= \sqrt{0.03^2 + 0.01^2} = 0.032 \\ Br2 &= \sqrt{0.02^2 + 0.01^2} = 0.022 \end{aligned}$$

$$= \frac{\ln \left| \dfrac{0.413 \pm 0.032}{0.079 \pm 0.022} \right|}{0.00193 \pm 0.00005}$$

$F1 = 0.032/0.413 = 0.0775$

$F2 = 0.022/0.079 = 0.278$

$Fr1 = \sqrt{0.0775^2 + 0.278^2} = 0.289$

$Z1 = 0.413/0.079 = 5.228$

$Br3 = (5.228)(0.289) = 1.509$

$$= \frac{\ln (5.228 \pm 1.509)}{0.00193 \pm 0.00005}$$

$\ln (5.228) = 1.654$

$Br4 = \ln (1 + Fr1)$
$= \ln (1 + 0.289) = 0.254$

$F3 = 0.254/1.654 = 0.154$

$F4 = 0.00005/0.00193 = 0.0259$

$Z2 = 1.654/0.00193 = 857.0$ s

$Fr2 = \sqrt{0.154^2 + 0.0259^2} = 0.156$

$Br5 = (857.0)(0.156) = 133.8$ s

Hence,

$$\begin{aligned} t_f &= Z2 \pm Br5 \\ &= 857.0 \pm 133.8 \quad \text{seconds} \\ &= 14.28 \pm 2.23 \quad \text{minutes} \end{aligned}$$

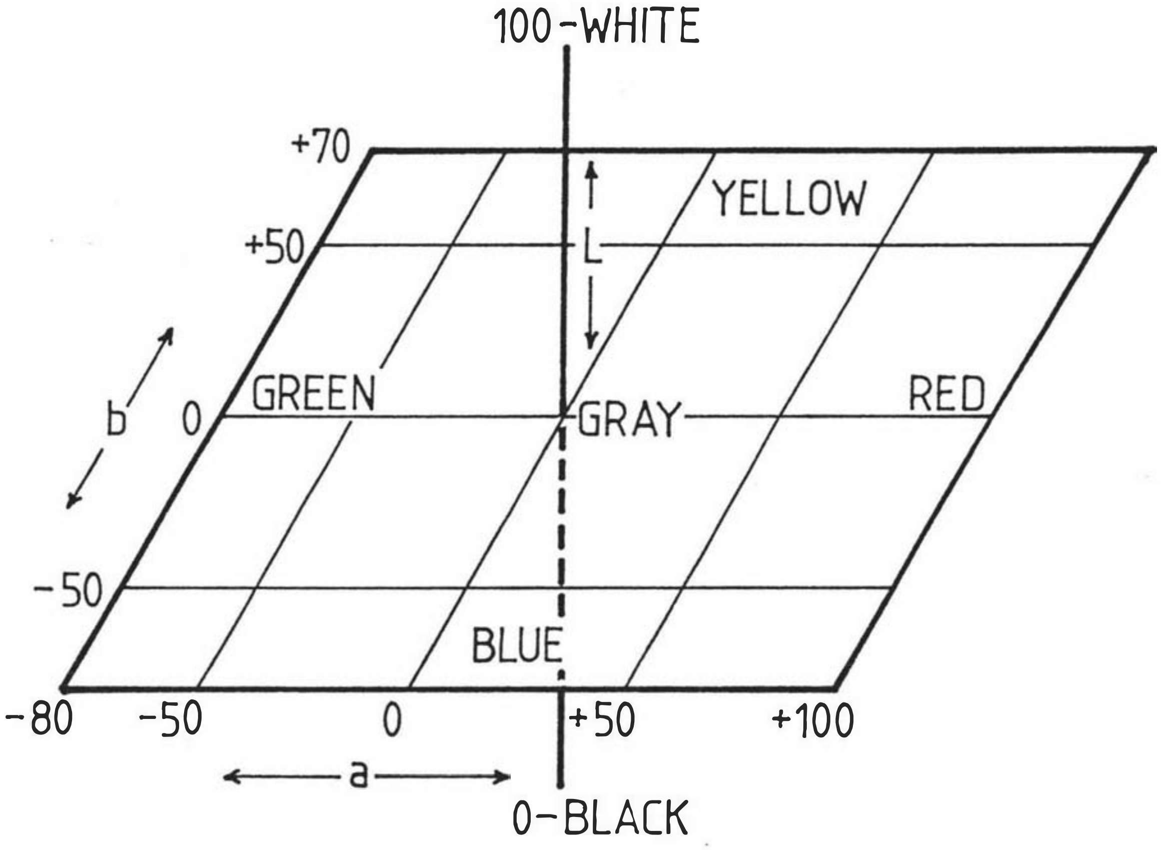
Solving for the overall drying time and 95% confidence bound,

$t_t = [1084.8 \pm 133.7] + [857.0 \pm 133.8]$ $\quad Br1 = \sqrt{133.7^2 + 133.8^2} = 189.2$ s

$$\begin{aligned} t_t &= 1941.8 \pm 189.2 \quad \text{seconds} \\ &= 32.36 \pm 3.15 \quad \text{minutes} \end{aligned}$$

APPENDIX 10.1

Hunter L-a-b Colour Solid[a]



[a] from Francis (1975b)

APPENDIX 10.2

Sample Calculations for the F-test Procedure

Using the procedure from Stoodley *et al.* (1980) on the solubility index of mineral acid casein from the factorial experiments on wet and dry samples,

Data:

Solubility of Sulph. Acid Casein

(deg. C) Temp.	(hr) Time	Moisture (% WB)	14		56
	1/3	.005	.005	2.229	2.088
60	2	.005	.005	2.398	2.539
	1/3	.005	.005	2.314	2.257
100	2	2.68	2.737	3.534	3.237

Treatment Comb.	Total	i	ii	iii	Est. Eff. iv=iii/8	Sum of Squares v=iii^2/16	Effect
(1)	.01	4.327	8.908	26.043			
a	4.317	4.581	17.135	15.149	1.893625	14.34326	A (M)
b	.01	4.947	8.868	7.495	.936875	3.510939	B (T)
ab	4.571	12.188	6.281	-3.319	-.414875	.6884851	AB (MT)
c	.01	4.307	.254	8.227	1.028375	4.230221	C (t)
ac	4.937	4.561	7.241	-2.587	-.323375	.4182856	AC (Mt)
bc	5.417	4.927	.254	6.987	.873375	3.051136	BC (Tt)
abc	6.771	1.354	-3.573	-3.827	-.478375	.9153706	ABC (MTt)
Total	26.043					27.1577	

Solve for:

C.F. = (Total^2)/16 = 42.38987

Sum SS = .005^2+.005^2+...-C.F.= 27.22493

Residual SS = Sum SS - Total SS = .0672345

ANOVA Table

Source	D.f.	S.S.	M.S.	F
A	1	14.34326	14.34326	1706.655
B	1	3.510939	3.510939	417.7545
C	1	4.230221	4.230221	503.3393
AB	1	.6884851	.6884851	81.92045
AC	1	.4182856	.4182856	49.77035
BC	1	3.051136	3.051136	363.044
ABC	1	.9153706	.9153706	108.9168
Residual	8	.0672345	.0084043	
Total	15	27.22493		

F value from Table

% Level Signif.	Value
5%	5.32
1%	11.26
0.1%	25.42

APPENDIX 10.3

Sample Calculations for the t-test Procedure

Using the procedure from Caulcutt (1983) on the solubility index of mineral acid casein from the factorial experiments on wet and dry samples,

Independent Variables:	Moisture Content (M) Storage Temperature (T) Storage time (t)
Dependent Variable:	Solubility Index (mL unsoluble/g dry solids)

RESULTS:

Sample Code	MC (% w.b.)	Temp. (C)	time (hour)	Solubility Index (mL unsoluble/g dry	SD solids)
1	14	60	.33	.005	0
2	56	60	.33	2.159	.0997
3	14	100	.33	.005	0
4	56	100	.33	2.286	.0403
5	14	60	2	.005	0
6	56	60	2	2.469	.0997
7	14	100	2	2.709	.0403
8	56	100	2	3.386	.21

CALCULATIONS OF EFFECTS:

```
M Effect = (S2+S4+S6+S8)/4 - (S1+S3+S5+S7)/4 MxT Int. = (S1+S4+S5+S8)/4 - (S2+S3+S6+S7)/4
           M =   1.894                                  =   -.415
T Effect = (S3+S4+S7+S8)/4 - (S1+S2+S5+S6)/4 Mxt Int. = (S1+S3+S6+S8)/4 - (S2+S4+S5+S7)/4
           T =    .937                                  =  -.3235
t Effect = (S5+S6+S7+S8)/4 - (S1+S2+S3+S4)/4 Txt Int. = (S1+S2+S7+S8)/4 - (S3+S4+S5+S6)/4
           t =  1.0285                                  =   .8735
MxTxt Interaction = (S2+S3+S5+S8)/4 - (S1+S4+S6+S7)/4
        MxTxt =  -.4785
```

Est. Residual SD = ((0^2+.0997^2+...+.21^2)/8)^(1/2) =.0916709

Test Stat. for MC = 2*Effect/RSD = 41.32175

Test Stat. for Temp = 2*Effect/RSD = 20.4427

Test Stat. for Time = 2*Effect/RSD =22.43898

Test Stat. for MxT = 2*Effect/RSD = 9.054132

Test Stat. for Mxt = 2*Effect/RSD = 7.05786

Test Stat. for Txt = 2*Effect/RSD = 19.05731

Test Stat for MxTxt = 2*Effect/RSD =10.43952

Critical Values from two-sided t-table with 8 df

% Signif. Level	Value
5%	2.31
1%	3.36
0.1%	5.04

APPENDIX 10.4

Results of the Multiple Regression Equation for Solubility Index (r^2=95%)

```
 The fitted equation is :
 Solind = -7.438 + 0.772*M - 0.019*M*M + 0.000*M*M*M - 0.000*T - 1.265*t
          + 0.022*T*t

Column          Coeff           SD(Coeff)         t-value
 constant         -7.438          2.166             -3.43
 M                 0.772          0.235              3.29
 M*M              -0.019        7.83E-03            -2.42
 M*M*M          1.47E-04        7.69E-05             1.92
 T            - 2.10E-04          0.010             -0.02
 t                -1.265          0.598             -2.12
 T*t               0.022        7.05E-03             3.11

the residual standard deviation about the model is S = 0.381

  with 18 - 6 = 12 degrees of freedom

R-squared =  94.54%

Analysis of Variance
Due to               SS        DF        MS=SS/DF
Regression         30.119       6          5.020
Residual            1.739      12          0.145
Total              31.858      18

Row          MC     Solind        yhat       residual     sd(yhat)      std res.

 1           14       0.005       0.053      -0.048        0.291         -0.13
 2           56       2.159       2.111       0.048        0.291          0.13
 3           14       0.005       0.337      -0.332        0.224         -0.87
 4           56       2.286       2.395      -0.109        0.228         -0.29
 5           14       0.005       0.139      -0.134        0.239         -0.35
 6           56       2.469       2.197       0.272        0.237          0.72
 7           14       2.709       1.886       0.823        0.229          2.16
 8           56       3.386       3.943      -0.557        0.231         -1.46
 9           14       0.996       1.012      -0.016        0.180         -0.04
10           56       3.089       3.070       0.019        0.180          0.05
11           30       2.596       2.691      -0.095        0.243         -0.25
12           30       3.088       2.889       0.199        0.222          0.52
13           30       4.054       4.438      -0.384        0.230         -1.01
14           30       3.475       3.565      -0.090        0.183         -0.24
15           56       3.326       3.014       0.312        0.179          0.82
16           43       3.327       3.258       0.069        0.357          0.18
17           30       3.742       3.509       0.233        0.174          0.61
18           19       2.455       2.288       0.167        0.211          0.44
19           14       0.579       0.957      -0.378        0.174         -0.99
```

APPENDIX 10.5

Hunter L-a-b colour values for mineral acid casein from the factorial experiments including the additional experiments on wet and dry samples.

Sample Code	Storage			Colour Values			Colour Index
	Moisture Content (% w.b.)	Temp (°C)	Time (hour)	L	a	b	
1	14	60	1/3	87.65^{c}	-2.17^{c}	6.83^{c}	276^{c}
2	56	60	1/3	87.42^{c}	-2.38^{c}	7.58^{c}	278^{c}
3	14	100	1/3	87.64^{c}	-2.39^{c}	7.67^{c}	281^{c}
4	56	100	1/3	87.69^{c}	-2.38^{c}	7.64^{c}	286^{c}
5	14	60	2	87.75^{c}	-2.12^{c}	6.94^{c}	286^{c}
6	56	60	2	87.45^{c}	-2.47^{c}	7.81^{c}	283^{c}
7	14	100	2	84.60^{c}	-0.66^{c}	13.03^{c}	1672^{c}
8	56	100	2	85.00^{c}	-1.68^{c}	9.40^{c}	478^{c}
9	14	80	2	87.69	-2.32	7.67	290
10	56	80	2	85.55	-2.35	7.92	288
11	30	60	2	87.01	-2.35	7.68	284
12	30	100	1/3	87.70	-2.39	7.68	282
13	30	100	2	84.57	-1.27	12.25	816
14	30	80	2	87.41	-2.42	7.95	287
15	56	100	1	84.98	-2.14	8.80	349
16	43	100	1	85.23	-2.18	8.70	340
17	30	100	1	86.45	-2.22	8.71	339
18	19	100	1	86.79	-2.26	8.80	338
19	14	100	1	87.27	-2.31	8.88	335
Control^{d}	14	---	---	87.2±0.6	-2.3±0.2	7.2±0.7	273±5

c average of 2 replications

d dried sample not exposed to any storage temperatures

APPENDIX 10.6

Results of the Multiple Regression Equation for Colour Index (r^2=61%)

```
 The fitted equation is :

 CI = 5925.10 - 142.65T + 0.87T*T - 1409.50t + 336.06t*t + 10.50Txt


Column           Coeff          SD(Coeff)          t-value
 constant        5925.10         2632.68             2.25
 T              -142.654          68.609            -2.08
 T*T               0.870           0.427             2.04
 t             -1409.50          618.428            -2.28
 t*t             336.059         221.146             1.52
 Txt              10.498           4.434             2.37

the residual standard deviation about the model is S = 241.416

  with 18 - 5 = 13 degrees of freedom

R-squared =  61.41%

Analysis of Variance
Due to                 SS        DF         MS=SS/DF
Regression          1.2E+06      5          241150
Residual              757661     13          58281.7
Total               2.0E+06     18


 Row        Temp    Colind        yhat       residual     sd(yhat)      std res.

  1          60        276      277.000       -1.000      170.707        -0.00
  2          60        278      277.000        1.000      170.707         0.00
  3         100        281      281.333       -0.333      139.382        -0.00
  4         100        281      281.333       -0.333      139.382        -0.00
  5          60        286      284.333        1.667      139.382         0.01
  6          60        283      284.333       -1.333      139.382        -0.01
  7         100       1672      988.667      683.333      139.382         2.83
  8         100        478      988.667     -510.667      139.382        -2.12
  9          80        290      288.333        1.667      139.382         0.01
 10          80        288      288.333       -0.333      139.382        -0.00
 11          60        284      284.333       -0.333      139.382        -0.00
 12         100        282      281.333        0.667      139.382         0.00
 13         100        816      988.667     -172.667      139.382        -0.72
 14          80        287      288.333       -1.333      139.382        -0.01
 15         100        349      340.200        8.800      107.964         0.04
 16         100        340      340.200       -0.200      107.964        -0.00
 17         100        339      340.200       -1.200      107.964        -0.00
 18         100        338      340.200       -2.200      107.964        -0.01
 19         100        335      340.200       -5.200      107.964        -0.02
```

APPENDIX 10.7

Calculations for Solving the Maximum Allowable Solubility Index for a Standard Acid Casein

GIVEN:

Sample: Acid Casein
Average Moisture Content: 12% (w.b.) = 13.64% (d.b.)
Maximum Allowable Volume of Insoluble: 0.02 ml
Amount of Sample Used in the Analysis: 10 g

SOLUTION:

Solving for the amount of dry solids available,

$$Wds = \frac{100\ Wws}{100 + MCdb} = \frac{100\ (10\ g)}{100 + 13.64}$$

$$Wds1 = 8.800\ g$$

$$Wds2 = 8.900\ g \quad (11\%\ w.b.)$$

$$Wds3 = 8.700\ g \quad (13\%\ w.b.)$$

From the experiments done on solubility of casein, the average total volume of dissolved casein on 0.5 N Sodium hydroxide was 88 ml and the volume of the centrifuge tube was 37 ml.

Solving for the amount of dry solids actually used in the test,

$$\frac{88\ ml}{8.800\ g} = \frac{37\ ml}{X}$$

$$X1 = 3.700\ g$$

$$X2 = 3.742\ g \quad (11\%\ w.b.)$$

$$X3 = 3.658\ g \quad (13\%\ w.b.)$$

Solving for the solubility index,

$$SI\ 1 = \frac{0.02\ ml}{3.699\ g} = 0.0054\ ml\ insoluble/g\ dry\ solids$$

$$SI\ 2 = 0.0053\ ml\ insoluble/g\ dry\ solids \quad (11\%\ w.b.)$$

$$SI\ 3 = 0.0055\ ml\ insoluble/g\ dry\ solids \quad (13\%\ w.b.)$$

Therefore the maximum allowable solubility index for a standard acid casein is approximately 0.006 ml insoluble/g dry solids

APPENDIX 10.8

Calculations using the t-test Procedure on Dry Casein

Independent Variables:	Moisture Content (M) Storage Temperature (T) Storage time (t)
Dependent Variable:	Solubility Index (mL unsoluble/g dry solids)

RESULTS:

Sample Code	MC (% w.b.)	Temp. (C)	time (hour)	Solubility Index (mL unsoluble/ g dry solids)	Standard Deviation
1	2.7	100	.33	.0015	.00071
2	6.7	100	.33	.0015	.00071
3	2.7	120	.33	.002	.00141
4	6.7	120	.33	.002	.00141
5	2.7	100	1	.002	.00141
6	6.7	100	1	.005	.00141
7	2.7	120	1	.005	.00141
8	6.7	120	1	.009	.00141

CALCULATIONS OF EFFECTS:

MC Effect =	.00175	MxT Interaction =	.00025
Temp. Effect =	.002	Mxt Interaction =	.00175
time Effect =	.0035	Txt Interaction =	.0015

M x T x t Interaction = .00025

Est. Residual SD = ((.00071^2+.00071^2+...+.00141^2)/8)^(1/2) =.0012717

Test Stat. for MC = 2*Effect/RSD = 2.752324

Test Stat. for Temp = 2*Effect/RSD =3.145513

Test Stat. for Time = 2*Effect/RSD =5.504649

Test Stat. for MxT = 2*Effect/RSD = .3931892

Test Stat. for Mxt = 2*Effect/RSD = 2.752324

Test Stat. for Txt = 2*Effect/RSD = 2.359135

Test Stat for MxTxt = 2*Effect/RSD =.3931892

Critical Values from two-sided t-table with 8 df

% Signif. Level	Value
5%	2.31
1%	3.36
0.1%	5.04