FOAM-MAT FREEZE DRYING OF EGG WHITE AND MATHEMATICAL MODELING

by

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February, 2007

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

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Eggs are a rich source of high-quality proteins as they contain all amino acids necessary for the human body. They also contain all vitamins (except for vitamin C) and many essential minerals. Eggs mainly consist of egg white (albumen) and egg yolk. Egg white is mainly made up of proteins and has excellent foaming properties; it is widely used in the baking and confectionary industries (e.g., cake mixtures, meringue).

Dehydration is widely used for the preservation of egg. Dehydrated egg products usually have a shelf life of one year under refrigeration. Spray drying and pan drying are widely used for producing egg powder. The higher drying temperature associated with these drying methods could adversely affect the nutritional value of egg. Freeze drying is well known for its excellent dehydrated product quality. The high cost of operation associated with freeze drying restricts its usage to high value products like coffee. Foam-mat drying can be used for the products that can be foamed to increase the surface area to improve the mass transfer rate. But the higher drying temperature involved in this method is not suitable for producing a high quality dehydrated product. Foam-mat freeze drying is one of the promising methods of drying, which tries to utilize the advantages of both freeze drying and foam-mat drying to produce better quality egg white powder.

Preliminary experiments showed that the stability of foams made with egg white alone is not adequate for foam-mat freeze drying. Experiments were thus conducted using different stabilizers (Methyl cellulose, Propylene glycol alginate and Xanthan gum) to optimize foam stability. Bubble size distribution was determined using microscopy to understand foam structure. The results showed that Xanthan gum at 0.125% provide sufficient stability for freeze drying. Experiments were conducted to study foam-mat freeze drying of egg white, in an effort to determine the suitability of this method. The results showed that the addition of Xanthan Gum during foaming has a positive impact in reducing the total drying time and also produces excellent quality egg white powder. The addition of stabilizer also plays an important role in improving drying. Heat and mass transfer models were applied for determining drying time and diffusion coefficients during freeze drying.

RÉSUMÉ

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Les œufs sont une bonne source de protéines de haute qualité, puisqu'ils contiennent tous les acides aminés nécessaires au corps humain. Les œufs contiennent aussi toutes les vitamines (à l'exception de la vitamine C), ainsi que plusieurs minéraux essentiels. Les œufs sont principalement constitués de l'albumine (blanc d'œuf) ainsi que le jaune d'œuf. L'albumine est principalement consituée de protéines et a d'excellentes propriétés de moussage. Elle est utilisée à grande échelle dans les industries boulangère et de la confiserie, par exemple dans les mélanges à gâteaux et de la meringue.

On utilise beaucoup la déshydratation pour préserver les oeufs. Réfrigérés, les produits d'œuf déshydraté se conservent pendant un an. Le séchage par atomisation et le séchange par conduction sont couramment utilisés pour produire de la poudre d'œuf. Par contre, les températures élevées associées à ces méthodes de séchage pourraient compromettre la valeur nutritive des œufs. La cryodessication donne un produit déshydraté de très haute qualité, mais les coûts d'opération élevés limitent son utilisation qu'aux produits de haute valeur, tel le café. Le séchage par émulsion peut être utilisé lorsque les produits à sécher peuvent mousser, ce qui accroît la surface de contact et augmente le coefficient d'échange thermique. Cependant, les températures élevées associées à cette méthode ne conviennent pas à la production d'un produit déshydraté de haute qualité. La cryodessication par émulsion est une méthode de séchage prometteuse, puisqu'elle tire des avantages liés à la cryodessication et au séchage par émulsion pour produire de la poudre d'albumine de meilleure qualité.

Des essais en laboratoire ont démontré que la stabilité des mousses de blanc d'œuf ne convient pas au séchage par émulsion. Des expériences ont donc été entreprises dans le but de trouver un stabiliseur pour les blancs d'œufs parmi la méthylcellulose, l'alginate de propylène glycol et la gomme de xanthane. Pour comprendre la structure de la mousse, la distribution de grandeurs de bulles a été déterminée en utilisant la micrographie. Les résultats démontrent que la gomme de xanthane en concentration de 0.125% a donné assez de stabilité à la mousse d'albumine pour la cryodessication par émulsion. Des expériences ont été entreprises pour déterminer la convenance de la cryodessication par émulsion pour déshydrater l'albumine. Les résultats démontrent que l'addition de la gomme de xanthane durant le moussage réduit le temps de séchage et produit une poudre de blanc d'œuf de haute qualité. L'addition du stabilisant aide alors à améliorer le processus de séchage. Des modèles de transfert de chaleur et de masse ont été appliqués pour déterminer le temps de séchage et les coefficients de diffusion durant la cryodessication.

ACKNOWLEDGEMENTS

I would like to thank Dr. Cristina Ratti, my thesis supervisor, for her support and encouragement throughout the course of this study. I would like to express my sincere gratitude to Dr. Vijaya Raghavan, my thesis co-supervisor, for his guidance, encouragement and support throughout my graduate studies.

I would like to convey my appreciation to Ms. Monica Araya for her help in conducting my experiments during my stay at Université Laval. My sincere thanks go to Mr. Yvan Gariépy for his help and time during the course of my studies. I would like to thank Dr. Rajkumar Perumal for his help and guidance in writing the thesis. I would like to thank Ms. Liette Connolly-Boutin for her help with the French abstract preparation.

I am grateful for the financial support from FQRNT, in the form of research grant for my project.

I would like thank my parents, my brothers and my sister-in-law's who are always there to support me. I would like to extend my gratitude to my friends Satya & Rajesh for their support, encouragement and friendship. I would like to thank Mr. Luis Felipe and his wife for helping me out with my accommodation during my time in Québec city. I would like to thank Narindhara Raharitsifa for his help during my stay at Université Laval.

I would like to thank Mrs. Susan Gregus, Mrs. Abida Subhan and Ms. Patricia Singleton for their help in administrative matters.

CONTRIBUTIONS OF AUTHORS

The work reported here was completed by the candidate and was supervised by **Dr. Cristina Ratti** of the Département des sols et de génie agroalimentaire, Université Laval, Sainte-Foy and **Dr. G.S.V. Raghavan** of the Department of Bioresource Engineering, Macdonald campus of McGill University, Montréal. The entire experiment was carried out at the Département des sols et de génie agroalimentaire. The authorship for the papers are 1) A. Muthukumaran, C. Ratti and G.S.V. Raghavan; 2) A. Muthukumaran, C. Ratti and G.S.V. Raghavan in Chapters IV and V, respectively.

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NOMENCLATURE

C_p	Heat capacity or specific heat, J/kg K
C_{SW}	Weight fraction of bound water in dried layer, kg of water/kg of solid
D	Diffusion coefficient or diffusivity m^2s^{-1}
$D_{win,e}$	Effective porous diffusivity of binary mixture of water vapour and inert gas in the dried layer, m^2/s
E_A	Activation energy,
J	Diffusion flux, mol m^{-2} s^{-1}
k	Thermal conductivity, W/mK
L	Height or thickness, m
m	Mass, kg
m_s	Latent heat of sublimation, kJ/kg
M_w	Molecular weight of water, mol
N_t	Total mass flux in the dried layer, kg/m^2s
N_w	Mass flux of water vapour, kg/m^3
P	Pressure, Pa
Per	Permeability, s
q	Heat flux, W/m^2
R	Universal gas constant $8.314X10^{-3}$ $kJmol^{-1}K^{-1}$
Ri	Radius, m
t	Time, s
T	Temperature, °C
V	Volume, kg/m^3
W	Fraction of initial water content remaining, %
x	Position, m
X	Amount of moisture, %
α	Thermal diffusivity, m^2/s
λ	Latent heat of sublimation, J/kgK
λ_{ice}	Latent heat of sublimation of ice, J/kgK
ρ	Density, kg/m^3

Φ	Concentration, mol m^{-3}
ΔH_s	Enthalpy of sublimation of frozen water, kJ/kgs
ΔH_v	Enthalpy of vaporization of sorbed water, kJ/kg

Subscript

c	Chamber
d	Dry
e	Effective value
f	Frozen
i	Interface
s	Solid
sat	Saturation
0	Initial
I	Dried region
II	Frozen region

I. GENERAL INTRODUCTION

1.1 Introduction

Protein is one of the important food components, essential to our body for maintaining fitness. Available protein from plant sources is minimal (except for soy bean) and they are relatively difficult to prepare into edible form without affecting the quality. Protein from animal sources is widely consumed all over the world and chicken egg is one of the most important sources of protein. Egg is consumed extensively in all regions and is part of many different delicacies. It is also a very good source of vitamins and minerals. All these attributes suggest that it is a wonderful supplement in a protein rich diet.

There are many technical difficulties in successfully transferring eggs from the point of production to the consumer. Egg is highly perishable and delicate in nature, which results in high levels of loss in handling and storage. The losses are mainly due to breakage, microbial spoilage, enzymatic and chemical reactions (Bergquist 1995). Different approaches have been tried to reduce the loss during handling and storage. One of the popular methods is dehydration. It has several advantages such as reduced product volume and making the product less susceptible for microbial and enzymatic spoilage among many other advantages.

Dehydration is also one of the oldest preservation methods. One of the U.S. patent on egg dehydration was issued in 1889 to Charles LaMont (Bergquist 1995). Pan-drying was a popular method for egg white drying. Before pan-drying, egg white is allowed to ferment by micro organisms naturally available on the egg shell. The

fermentation removes glucose from egg; if glucose is not removed from egg white it can increase the spoilage of egg white powder during storage because of enhanced oxidation. Removal of glucose to improve the properties of egg white powder by reducing insolubility, it also helps to avoid browning or discolouration by preventing the reaction between glucose and amino groups of protein (Shehab et al. 1978). Belt drying method has been used for drying whole egg in China in early 1990's, which is a continuous process. Increased demand for eggs during World War II, lead the research initiatives in egg dehydration. Spray drying of egg was developed in early 1940's and it is still one of the popular methods for eggs drying. Some of the problems associated with dehydration of eggs are change in colour, denaturisation of proteins, and poor rehydration quality.

Freeze drying is a drying method often credited for its excellent product quality and stability. Structural integrity and the preservation of volatile components results in excellent quality of the freeze dried product. It is a method for removing moisture through sublimation. This is achieved by keeping the conditions of water below that of triple point through combination of temperature and pressure (Jafar & Farid 2003).

The rehydration properties of freeze dried products are excellent. The colour and other quality losses are very minimal. However, the high operation and set up costs restricted the use of freeze drying for only high quality/value products such as coffee and pharmaceutical products. Intensive research is needed to study and understand the freeze drying process, which can help in reducing its cost.

Foam-mat drying is a method of drying, which increases the surface area available for drying by foaming the product to be dried and thus drying times are markedly reduced. Other advantage in foam-mat drying includes better quality final

product as the drying temperature is less than conventional drying methods and improvement in drying rate. It has been only a lab curiosity method of drying, but has a greater potential to solve many of the problems associated with drying.

Building prototype dryers often costs more, which is one of the inhibiting factors in freeze drying research. Creating mathematical models to describe heat and mass transfer properties during freeze drying under various conditions is one of the better alternatives to overcome some of the problems associated with drying research. Mathematical modeling has become one of the important tools available for today's researchers. The availability of computing power at lower cost has enabled construction of complex models, which requires enormous computing power to solve. Mathematical models can help to understand the physical phenomena without conducting real experiments. Heat and mass transfer models developed using mathematical approach can help us in designing freeze drier and optimizing drying conditions.

Egg white (or egg albumin) has been traditionally used in bakery industry for its excellent foaming properties, which makes it one of the better candidates for foam-mat drying. As freeze drying can produce very good quality product, it would be appropriate to combine foam-mat and freeze drying for foam-mat freeze drying of egg white. By applying this method we could reduce freeze drying time to reduce the cost of freeze drying. As the surface area is increased by foaming we could expect shorter drying time with foam-mat freeze drying than conventional freeze drying. However the use of foaming could affect the dryer load, as the density is significantly reduced by foaming. The effect of foaming on overall cost of operation has to be studied to understand the drying operations and its suitability for producing egg white powder. This study mainly

focuses on determination of drying time for foam-mat freeze drying of egg white and developing a simple model for predicting drying time.

1.2 Hypothesis

This work is aimed at developing a mathematical model for foam-mat freeze drying of egg white. In freeze drying one of the biggest problem is longer drying times. The hypothesis is that when we create foam it will increase the surface area where by increasing overall mass transfer. This could improve the freeze drying by reducing the drying time while producing better quality product.

This work is aimed at determining drying time for foam-mat freeze drying of egg white. Simple model was also developed for predicting the drying time and the results were compared with actual data obtained from experiments.

II. GENERAL OBJECTIVES

2.1 Objectives

The overall objective of the project was to study foam-mat freeze drying of egg white, which is a part of the diet of millions of people all over the world and one of the most perishable and delicate food material. The specific objectives of the project are:

1. To optimize foam stability of egg white for freeze drying
2. To study drying kinetics of egg white by foam-mat freeze drying
3. To model foam-mat freeze drying of egg white using heat and mass transfer equations

2.2 Scope

Present study will be focusing on foam-mat freeze drying of egg white. The methodology can be applied for different products but proper research has to be conducted to determine specific requirement for each product. The stabilizers chosen and their concentration may not be suitable for other products, hence further research is needed to determine requirement for each products individually.

III. LITERATURE REVIEW

3.1 Overview of Egg Processing Industry in Canada

According to FAO statistics (2006), the global egg production during 2005 was 59.3 million metric tonnes. Global egg production and processing related industries have a value of more than $5 billion. According to Statistics Canada (2006), the annual Canadian egg production (whole egg) was 1,200,000 (in numbers) for 2005. The production of dried egg (dried whole egg, dried egg yolk and dried egg albumen) was 3,800,000 kg. Canadian egg production with respect to world egg production is shown in Table 3.1. The egg production in Canada has been increasing gradually over a period of time (Figure 3.1). Though Canada's share in worldwide egg production and processing looks small, the value of the industry within the country is significant. The value of Canadian egg industry is estimated at $ 600 million (Statistics-Canada 2006).

Advances in technologies and commercial standards have forced egg industry to be competitive. The increase in demand and need for providing better quality product to consumers at lower price has been driving the technological innovations in egg industry. For example, increased demand during World War II led the research initiative during that time, which resulted in the development of many dehydration methods, noticeably spray drying method. Even today, spray drying is one of the popular choice for processors in order to produce good quality egg powder (Bergquist 1995).

When it comes to the international market, the quality of the product is of paramount importance. Eggs are highly perishable and delicate in nature. Reducing handling and storage losses are also very important for processors to remain competitive.

These are some of the driving factors in developing new technologies and optimizing existing technologies to stay ahead in the market.

Table 3.1 World Egg production (FAOSTAT Data 2006)

	Hen Eggs Production (Mt)					
	2000	**2001**	**2002**	**2003**	**2004**	**2005**
World	51,693,563	53,286,096	55,199,731	56,757,479	58,057,493	59,251,063
Canada	372,390	385,330	391,540	392,780	376,560	399,015
China	19,432,880	20,229,700	21,287,900	22,509,170	23,501,250	24,348,250
India	2,013,000	2,151,000	2,217,000	2,371,000	2,464,000	2,492,000
USA	4,998,300	5,086,100	5,164,900	5,180,200	5,278,300	5,329,600

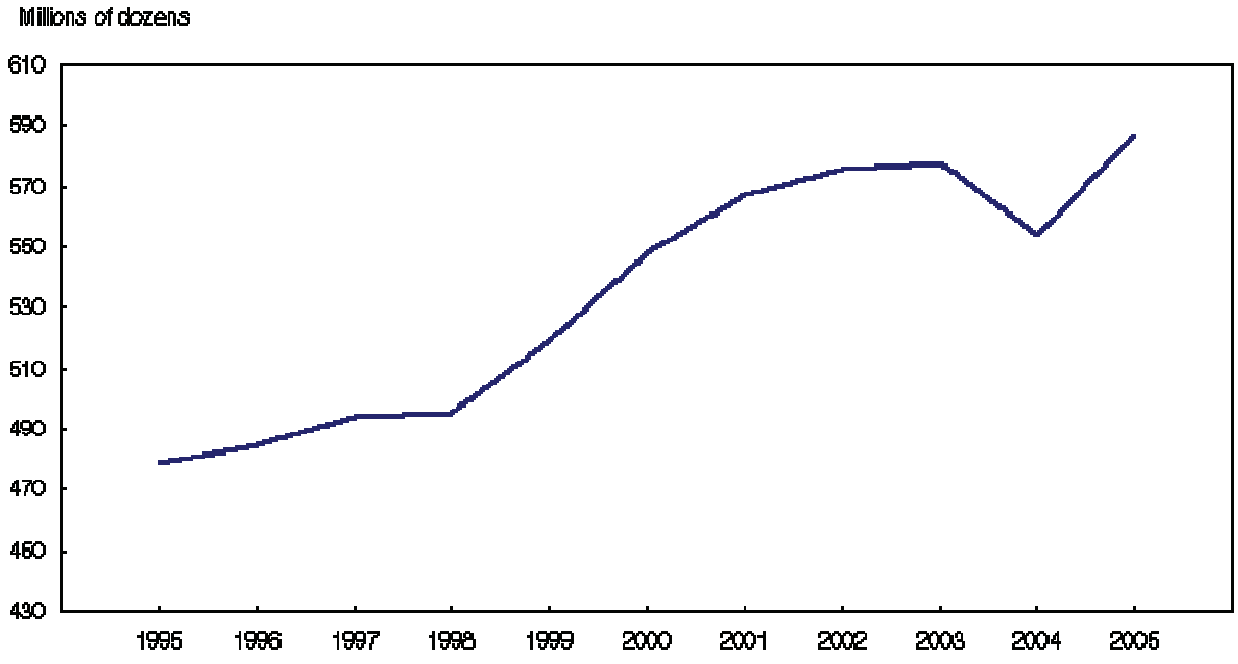

Figure 3.1 Egg Production in Canada between 1995 and 2005 (Statistics-Canada 2006)

3.2 Structure and composition of egg

A chicken egg primarily consists of the following parts:

i) Shell

ii) Membrane

iii) Albumen

iv) Yolk

The proximate composition of egg is given in the Table (3.2). Albumen or egg white is the single largest component of an egg, which represents about 60% of total weight of the egg (Froning 1998). Albumen is rich in protein; ovalbumin is the major protein of egg white; which accounts for 54% of total proteins present in albumen (Table 3.3).

Some of the previous research works show that eggs have antioxidant effect. This property has been attributed to conalbumin (or Ovotranferrin). Research has to be done to determine the true potential of egg white as an antioxidant (Froning 1998). This can be an important property which could have great impact on the food processing industry as they are looking for natural ingredients in order to produce healthy, chemical free foods.

3.3 Foams

In food processing operations we encounter different kinds of foams, some of them are desirable (for example egg white foam in bakery products) and in some cases, it may not be desirable (for example foaming during fermentation process). Foams provide unique texture to many of our food products, for example bread, cake and ice creams. Understanding the nature of the foam and its physical properties are important to have good control over them (Foegeding et al. 2006).

Foam is a two phase system having a dispersed phase (usually air) and a continuous phase. Dispersed phase is larger than the continuous phase (German & Phillips 1994; Baniel et al. 1997). Based on the ratio of dispersed phase to continuous phase, foams can be classified into polyhedric foam and dilute bubbly foam. In polyhedric foams the ratio is large; which results in large number of bubbles. As the number of bubble increase they press each other to form honeycomb structure. Egg white foam and beer foam can be good examples for polyhedric foams. In dilute foams the ratio is small; hence individual bubbles retain their spherical shape. Choco-mousse can be a good example for dilute bubbly foams (Prins 1988).

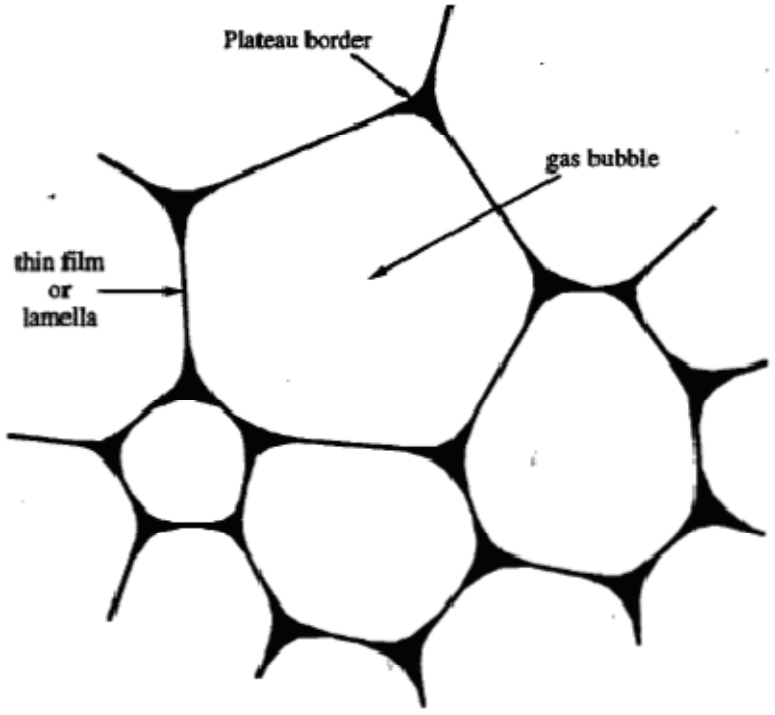

Figure 3.2 Structure of foam (Wilde & Clark 1996)

Table 3.2 Nutrient Composition of egg (per 100 g) (Britannica 2007)

	Whole egg	Egg white	Egg yolk
Energy, kcal	149	50	358
Water, g	75.33	87.81	48.81
Protein, g	12.49	10.52	16.76
Fat, g	10.02	0	30.87
Cholesterol, mg	425	--	1,281
Carbohydrate, g	1.22	1.03	1.78
Vitamin A, IU	635	--	1,945
Riboflavin, mg	0.508	0.452	0.639
Calcium, mg	49	6	137
Phosphorus, mg	178	13	488

Table 3.3 Egg white proteins (Li-Chan et al. 1995; Froning 1998)

Protein	% of albumen proteins	Characteristics
Ovalbumin	54	Phosphoglycoprotein
Ovotranferrin (Conalbumin)	12	Binds metallic ions
Ovomucoid	11	Inhibits trypsin
Ovomucin	3.5	Sialoprotein, viscous
Lysozyme	3.4	Lyzes proteins
Globulins	8.0	---
Ovoinhibitor	1.5	Inhibits serine proteases
Ovoglycoprotein	1.0	Sialoprotein
Ovoflavoprotein	0.8	Binds riboflavin
Ovomacroglobulin	0.5	Strongly antigenic
Cystatin	0.05	Inhibits thiol proteases
Avidin	0.05	Binds biotin

3.3.1 Theory of foam formation

Proper understanding of mechanism involved in foam formation is important to make foam with required characteristics. Foams have gas bubbles surrounded by plateau border (Fig. 3.2). The thin wall of a bubble is called lamella. The mechanical strength of lamella determines the stability of the foam along with their air/water interface properties. If viscous liquids are used for foam making, they usually produce more stable foams; this is due to the increased elasticity of the lamella. The stability of the foam can be restored by using surfactants (surfactant-stabilize foams) or by proteins (protein-stabilized foams). The mechanism involved in retaining or improving the stability of the foam for these two (surfactant and protein) are different. Surfactants diffuse through and strengthen the thin lamella to give more stability to the foam. The mechanism is known as Marangoni effect (Wilde & Clark 1996).

Proteins are adsorbed at the film interface and interact with lamella in many ways and forms electrostatic, hydrophobic, covalent and hydrogen bonding; this increases the stiffness and viscoelasticity of lamella to increase the stability. The mechanism involved with protein based stabilization is known as viscoelastic mechanism of stabilization (Wilde & Clark 1996).

Formation of foam depends on many parameters such as the properties of the liquid being foamed, method of foaming and foaming conditions. For protein based foams, the adsorption of protein during foam formation must be rapid to have better foamability. The adsorption of protein can be described by three processes. First, protein is transported from the liquid to the interface during foam formation; second, protein penetrates into lamella and then finally, it interacts with lamella to improve the stability.

The transportation of protein occurs mainly by diffusion or convection and/or by combination of both these methods. The type of protein present in the sample plays a major role in determining the type of foam and its stability. For example in case of egg white presence of albumen gives an excellent foaming characteristics (Wilde & Clark 1996; Pugh 2001).

3.3.2 Egg white foam

Egg white is one of the important ingredients in many of our bakery products. Its popularity in bakery industry can be attributed to its ability to form relatively stable and voluminous foam. One form of egg white foam, known as meringue, is the starting part of many of the aerated foods. As seen in Table 3.3 egg white foam is rich in albumen (egg white protein), which plays a major role in providing relatively stable foam. The presence of protein is one of the major reasons for the relatively stable and voluminous foam, as the protein will be adsorbed at the air – liquid interface (Alleoni & Antunes 2004; Foegeding et al. 2006).

3.3.3 Formation of foam – different methods

Foam formation depends on many parameters, such as the composition of the liquid, foaming method used, temperature and duration of foaming. The method of foaming determines the quality and quantity of foam. Based on the amount of air added and method of addition, foaming can be classified into i) addition of unlimited amount of air to limited amount of liquid (for example, shaking and whipping) ii) addition of limited amount of liquid with limited amount of air (ex., sparging) iii) in-situ bubble development in the liquid (ex. bread baking). Addition of limited amount of air to limited

amount of liquid gives precise control over the foam formation but the complexity involved in operation makes it less adaptable for industrial application. The first method (unlimited amount of air to limited amount of liquid) is popular because of its ease of operation and is widely used in foam making (Prins 1988; Van Kalsbeek & Prins 1999).

3.3.3.1 Shaking

In this method, agitating the liquid vigorously results in the formation of foam. The volume of the foam formed depends on many parameters like the amplitude and frequency of shaking, the volume of the liquid taken, shape of the container, protein content of the liquid and temperature. This method is not commonly practiced on large scale foam production (Halling 1981; German & Phillips 1994).

3.3.3.2 Whipping

In whipping unlimited amount of air is added to limited amount of liquid to make foam. This is one of the most common methods of foam making and is widely used in food processing industry. In this method, air is trapped inside the liquid due to the action of an agitator. When trapped inside the liquid, the size of the air bubble will be large and is subsequently broken into small bubbles due to the mechanical agitation. The final size of the bubble depends on the speed of the agitator, the geometry of the apparatus and the rheological properties of the liquid. Poor design of the agitator can greatly affect the foaming process after initial period of foaming. If the agitator become completely covered by the foam, it could prevent further addition of air to the system (Prins 1988; German & Phillips 1994).

3.3.3.3 Sparging or Bubbling

The method involves injecting a known amount of air through an orifice into a known quantity of liquid. The size of the bubble formed highly depends on the viscosity of the liquid. This method has greater control over the size of bubble achievable by adjusting the diameter of the orifice. It is commonly used for basic foam studies, because of the bubble uniformity obtained from this method (Halling 1981; German & Phillips 1994).

3.3.4 Stability of foam and different mechanisms of foam stability

Foams are highly fragile in nature, which makes the study of foams very difficult. The change occurring inside the foam is so dynamic, in some cases even within a minute there can be a drastic change. Determination of foam stability is important, and is the first step in studying foam properties. Most of the foams used in food processing have some form of protein as their major component. The type of protein and their interactions with the aqueous phase can play a major role in determining the life of foam (Foegeding et al. 2006).

A typical volume profile of foam during and after formation is shown in the Figure 3.3. High levels of surface energy are created by large air-water interfaces and the density difference between two phases makes foams thermodynamically unstable. The main mechanisms that contribute to the destabilization of foam are drainage of liquid phase and mass transfer across foam lamellae. The mass transfer results in the thinning of the walls of the bubble, which eventually leads to rupture. In case of polyhedric foams the capillary pressure within the foam system is high due to smaller bubble size, which results in the diffusion of adjacent small bubbles and formation of bigger bubbles; this

renders the foam unstable. The interfacial viscoelasticity of the lamellae can play a major role in helping to stabilize the foam by reducing the drainage and giving more mechanical strength to the bubbles (Heller & Kuntamukkula 1987; Fruhner et al. 2000).

In polyhedral foams, three lamellae films join to form plateau border (Fig 3.2). These plateau borders form the edges of a gas bubble and play an important role in foam stability. Each bubble has four edges and they tend to join at equal angles (approximately 109.47°), this constraint is a basis for curved films of gas bubble, which also results in complicated shapes. Curved films help to balance the tension on bubble by reducing surface energy (Kraynik 1988).

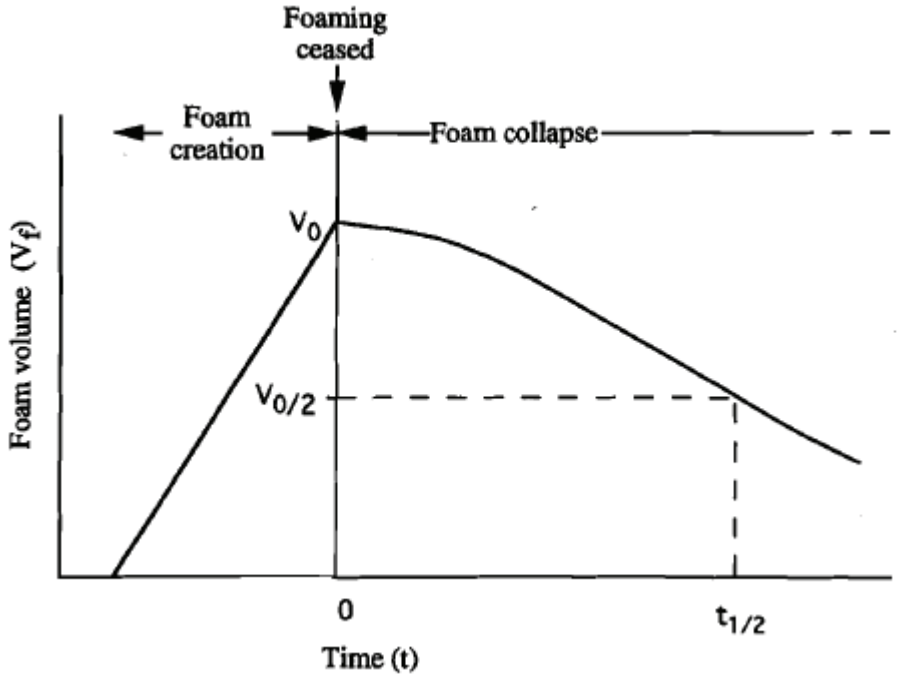

Figure 3.3 A typical foam volume profile during and after formation (Wilde & Clark 1996)

Protein based foams are relatively stable. The stability of protein based foams like egg white foam depends on many factors like protein concentration, pH, ionic strength, intermolecular interaction, temperature, presence of salts, film thickness and surface viscoelasticity. The presence of protein at the air – liquid interface rapidly reduces interfacial surface tension, this helps to stabilize the foam. The rheological properties at the interface are also important and should be taken in to consideration when studying foam stability (Wilde & Clark 1996; Murray 2002; Alleoni & Antunes 2004; Foegeding et al. 2006).

Stability of foams can be determined by many factors like drainage, film rupture and disproportionation of bubbles. Drainage method is widely used for the determination of foam stability. This is done by measuring the height of foam over a period of time or by measuring the liquid drainage from foam over a period of time from the time of foam formation. More extensive work on stability of foam can be found in the literature (Prins 1988; German & Phillips 1994; Wilde & Clark 1996).

3.4 Foam stabilizers

For foam to have a reasonable life it should have some kind of surfactants or foaming agents or stabilizers in their continuous phase. Foam stabilizers basically increase the interfacial viscoelasticity of foam lamellae, which subsequently increase the stability of the foam (Heller & Kuntamukkula 1987). The viscoelasticity mechanism of foam stabilization alone cannot explain the effect of stabilizers on foam stability and it needs more research for proper understanding (Fruhner et al. 2000).

The advancement in increasing foam stability was more of a trial and error method, for example some researchers claimed that egg white foam produced on copper

bowl has higher stability than those made using another kind of bowl. This claim indicates the effect of copper on the stability of foam (Sagis et al. 2001). Similarly different kinds of stabilizers are used in stabilizing foams and emulsions. Most of the stabilizers are high molecular polysaccharides in nature. Their hydrophobic nature prevents them from being absorbed at the plateau borders, this helps to strengthen bubble walls, which in turn helps to improve the stability of the foam (Papalamprou et al. 2005). Polysaccharides are more popular type of stabilizers than any other types (Baeza et al. 2004). Proteins can also be used as stabilizers. For a protein to be a good stabilizing agent it should be able to reduce the surface energy levels between the bubbles as they are continuously created during foaming (German & Phillips 1994).

3.4.1 Xanthan Gum

Xanthan gum is one of the widely used polysaccharide in food processing industries. *Xanthomonas campestris* pv. campestris produces Xanthan, which is exopolysaccharide in nature. Polyelectrolyte nature of the Xanthan molecule makes it highly water soluble. The temperature of the water does not affect the solubility of Xanthan gum; this makes it highly adaptable for industrial applications regardless of the processing temperature (Becker et al. 1998).

Xanthan Gum is one of the extensively researched food additives for its toxicological and safety properties. Laboratory tests at USDA on rats, showed no adverse effects such as toxicity and growth inhibition. Long term studies on rats and dogs also proved Xanthan gum produces no adverse effect (Kang & Pettitt 1993). United States Food and Drug Administration (FDA) approved Xanthan gum in 1969 as a food additive without any specific quantity limitations. In 1980 it got the European Commission (EC)

approval (Kang & Pettitt 1993; Katzbauer 1998; Garcia-Ochoa et al. 2000). It also got Canadian Governor-in-Council approval. The physical properties of Xanthan Gum are shown in Table 3.4 (Kang & Pettitt 1993).

When Xanthan gum is added to any liquid it increases the viscosity of the liquid, due to this property it is widely used in food industry as a thickening agent as well as stabilizer. It can produce very high viscosity at lower concentration, for example at 1% level it can produce viscosity in the range of 1000 – 4300 mPa s. Viscosity of the solution is dependent on many factors such as temperature, pH, concentration of Xanthan gum and concentration of salts. The effect of heat and pH on affecting the performance of Xanthan Gum is usually minimal (Lachke 2004; Sahin & Ozdemir 2004).

3.4.2 Propylene Glycol Alginate

Propylene glycol alginate (PGA) is a surface active ester obtained from alginic acid. It is a high molecular weight 1, 4 D-mannuronic acid and L-guluronic acid (Baeza et al. 2004). It increases the viscosity of the solution, which will help improving the stability of foam by reducing the drainage. Its cross linking ability was investigated in studies involving model foam. The experiments on thin film drainage by Wilde and Sarkar (1999) showed that PGA improved the stability of foam; but when the concentration level of PGA was increased fluid drainage increased. The increased drainage by PGA at higher concentration has not been properly explained.

3.4.3 Methyl Cellulose

Methyl cellulose is another popular food additive, which is widely used in food processing industries. It is a cellulose derivative; cellulose ethers are produced by etherification of alkaline cellulose with methyl chloride. It produces a gel upon heating,

which is completely reversible. This property is unique, which make it popular for many different food preparations. The surface active nature of methyl cellulose imparts the stability, when added to a foam (Karim & Wai 1999). Methyl cellulose is also used to make edible coatings (Arvanitoyannis & Biliaderis 1999; Maftoonazad & Ramaswamy 2005).

3.5 Drying

Drying or dehydration is one of the oldest and popular preservation methods. Records indicate that drying of vegetables was practiced as early as 18th century. Still it is one of the major fields in food processing operations. Development in drying has been gradual and it addresses issues on industrial requirements. During World War periods (both first and second) the research and development got greater impetus because of the greater requirements. During drying simultaneous heat and mass transfer takes place, this imparts changes in the dried product. Drying and dehydration are often used alternatively without much of difference. But they are not same, according to US Department of Agriculture; dehydrated food cannot have moisture content above 2.5% on dry basis. But dried food can have moisture content above 2.5% (dry basis). Different kind of dryers have been developed to address specific requirements such as solar drying, drum drying, spray drying, spouted bed drying, fluidized bed drying, microwave drying and freeze drying (Mujumdar 1995; Vega-Mercado et al. 2001)

Table 3.4 Physical properties of commercial Xanthan gum (Kang & Pettitt 1993; Garcia-Ochoa et al. 2000)

Property	Value
Physical state	Dry, cream-colored powder
Moisture (%)	8 – 15
Ash (%)	7 – 12
Nitrogen (%)	0.3 – 1
Acetate content (%)	1.9 – 6.0
Pyruvate content (%)	1.0 – 5.7
Monovalent salts (g L^{-1})	3.6 – 14.3
Divalent salts (g L^{-1})	0.085 – 0.17
Specific gravity	1.6
Bulk density, kg/m3	839
Browning temperature, °C	160
Mesh size (Tyler standard)	40
Surface tension, dyn/cm	75
Freezing point, °C	0.0
Viscosity (cP)	13 – 35
(15.8 s^{-1}, C_p = 1 gL^{-1}, T_D = 25°C, T_M = 25°C)	

3.6 Freeze drying

Freeze drying or lyophilisation was first introduced in the forties for large scale production of dry plasma and blood products (Vega-Mercado et al. 2001). Freeze drying is one of the drying methods, which can produce high quality dried product. Freeze drying has two important steps; one is freezing of the material and then drying under vacuum. This method takes advantage of triple point of water. Triple point is a state in which substances coexists in different states such as solid, liquid and vapour and remain in thermodynamic equilibrium. Water has triple point at 0.01 °C and 611.73 Pa (Figure 3.4) (Geankoplis 1993). Below triple point (temperature and pressure combination) ice can be directly converted to vapour, a process known as sublimation.

Some of the advantages of freeze drying, which makes it an attractive process are (Liapis & Bruttini 1995; Liapis & Sadikoglu 1997; Vega-Mercado et al. 2001; Jafar & Farid 2003),

i) The absence of air during processing prevents oxidative and chemical deterioration of the product

ii) Lower drying temperature, which preserves volatile and flavour components

iii) Absence of moisture movement within the material during drying and

iv) Dried product has excellent re-hydration properties

Freeze dried food products have low density and higher nutritional value, which makes a popular choice for astronauts and mountaineers. The drying time is usually longer, which results in higher cost of drying. During freeze drying the temperature of the condenser and vacuum level should be maintained to the lowest possible value and this also contributes towards increased drying costs. This is one of the major reasons its

use is restricted only for high commercial value products like pharmaceutical and coffee (Vega-Mercado et al. 2001; Jafar & Farid 2003; Khlloufi et al. 2005).

Some researchers have tried to optimize the drying conditions (condenser temperature and vacuum level) for various products, so as to reduce overall drying time and energy consumption (Jafar & Farid 2003). Still, construction of lab scale freeze drier itself can be expensive, which is one of the major factors affecting the research and development in this field. A better alternative could be to develop mathematical models to describe freeze drying.

3.6.1 Principles of freeze drying

In freeze drying process, the material is first frozen completely to convert moisture into ice. After complete freezing, the material is placed inside the drying chamber, where the pressure is reduced to create vacuum. After the required amount of vacuum is reached, the temperature of the shelf is gradually raised to supply the necessary heat for latent heat of sublimation. Phase diagram of water is presented in the Figure 3.4, from which it can be seen that when the proper conditions are maintained, ice can be directly vaporized or sublimated; freeze drying takes advantage of this property of water and works on the same principle (Karel 1975).

Freeze drying has three distinct phases; freezing, primary drying stage and secondary drying stage. Drying is faster during primary drying state due to the availability of large amount unbound water in frozen state. During secondary drying stage, bound water has to be dried. Major portion of the bound water will be in unfrozen state and the drying rate will be very slow (Figure 3.5) (Mellor 1978; Vega-Mercado et al. 2001).

3.6.1.1 Freezing

Freezing is one of the important steps if freeze drying. The freezing of the product can be achieved either within the freeze drying apparatus or in a separate freezing chamber and the choice mainly depends on the cost and operating methods used. Freezing has some important functions like, partial dehydration and increasing the rigidity of the structure. Freezing temperature should be much lesser than that of freezing temperature of pure water as water is mostly present in the combined form. The most common freezing temperature is – 30 °C. During freezing most of the free water is completely frozen and only bound water remains unfrozen. (Flink & Knudsen 1983; Liapis & Bruttini 1995).

During freezing the rigidity of the material increases due to ice formation and this may not be uniform throughout the frozen material. This is due to the presence of bound water, which remains unfrozen. These unfrozen regions are supported by the surrounding ice, which prevents deformation of the product to some extent. The method of freezing (quick freezing or slow freezing) can play a major role in determining the structural integrity of the product during freezing (Mellor 1978; Flink & Knudsen 1983; Liapis & Bruttini 1995).

3.6.1.2 Primary drying Stage

During primary drying, the frozen water is removed by sublimation. To achieve drying during primary stage the pressure inside the drying chamber must be less than or in equilibrium with the vapour pressure of the frozen water. For pure water the absolute pressure should be 4.58 mm Hg or less at 0 °C (Figure 3.4). For practical drying applications the temperature and pressure combination must be lower than that of pure

water to achieve drying. The lower pressure and temperature combination is necessary because water mostly exist in combined form. The average value of pressure and temperature during freeze drying are 2 mm Hg or less - or 10 °C and less, respectively (Flink & Knudsen 1983; Liapis & Bruttini 1995).

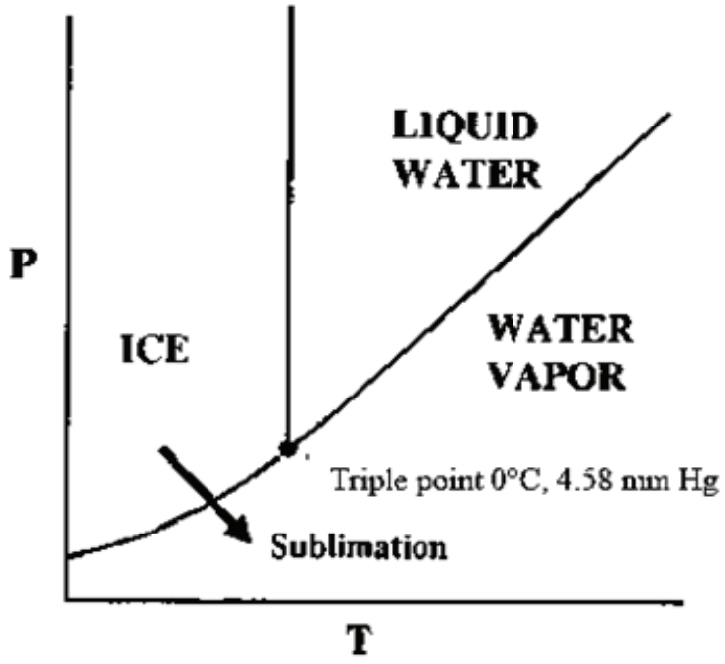

Fig 3.4 Sublimation of ice during freeze drying (Karel & Lund 2003)

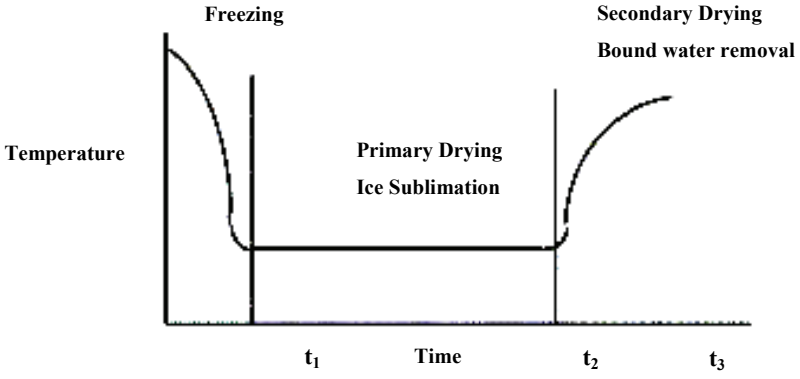

Fig 3.5 Different phases of freeze drying (Mellor 1978; Vega-Mercado et al. 2001)

To achieve drying we need to supply latent heat of sublimation (for ice at 0 °C this is 2840 kJ/kg (Flink & Knudsen 1983; Liapis & Bruttini 1995)). During sublimation, latent heat is absorbed which results in the temperature reduction in the frozen layer. If there is no heat input, the water vapour pressure of the frozen product comes into equilibrium with the drying chamber and there will be no further sublimation. The latent heat supply can be achieved either by conduction, convection or radiation. During freeze-drying, conduction and radiation heat transfers are more common than convection. The amount of heat that could be supplied without affecting the product is one of the limiting factors in freeze drying. One of the important limiting factors for heat input is the maximum temperature the frozen layer could withstand and remain frozen. Melting of frozen layer can have adverse effect on the product quality in many ways. Collapse can occur, which results in structural deformation of the dried product. Some other factors which affect the maximum heat input are colour sensitivity of the product, biosensitivity of the product and structural deformation in the dried product (Mellor 1978; Flink & Knudsen 1983; Liapis & Bruttini 1995).

Usually the sublimation of water starts at the surface and water vapour is directly removed. After some time of drying, the product will have two distinct layers: the ‘Dry layer’ and the ‘Frozen layer’. Once a dry layer is formed, the water vapour is transferred through it. In ideal drying conditions both layers can be distinguished properly (Figure 3.6 (a)). But in practical drying conditions that may not be the case, usually there will be a transition layer between frozen and dry layer (Figure 3.6 (b)). The end of the primary drying stage is marked by a sharp decrease in drying rate. By the end of the primary

drying stage, all the free water available is sublimated. (Karel 1975; Flink & Knudsen 1983; Liapis & Bruttini 1995).

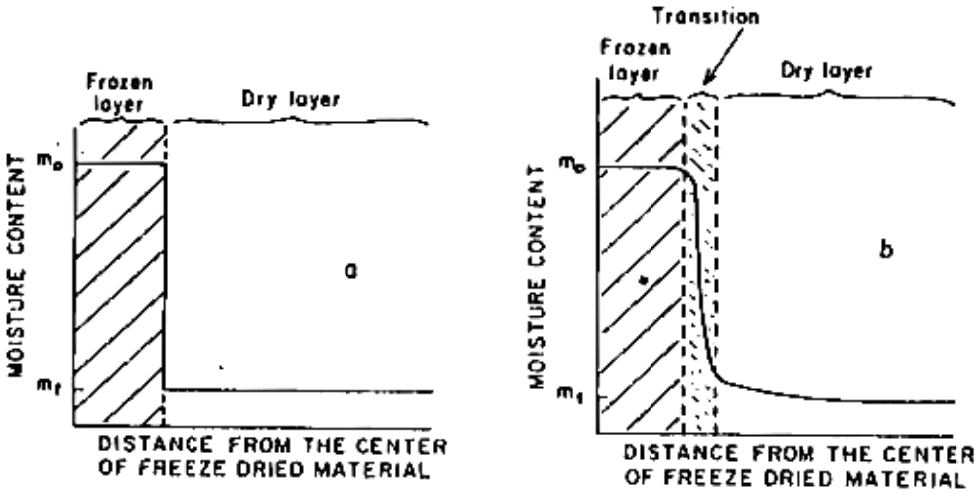

Figure 3.6 Dry layer and Frozen layer during ideal (a) and practical (b) conditions (Karel 1975)

3.6.1.3 Secondary drying stage

Some of the bound water, which remains unfrozen, may be taken up by the dry layer and this process is known as sorption. Sorption of bound water makes the product unstable in terms of structural and chemical stability and it can also adversely affect the drying rate. The method of removal of bound water is known as desorption and this comes under secondary drying stage. The presence of bound water can be attributed to physical and chemical adsorption as well as water of crystallization (water present in crystalline framework of ice crystal, which doesn't freeze drying freezing). On an average the amount of bound water is between 10 and 35% of the total moisture content. In ideal drying conditions the secondary drying stage starts after primary drying stage and both can be distinguished. In practical drying, these two stages are overlapped. Some

of the bound water is removed during the primary drying stage itself. But for calculations it is assumed that primary drying stage ends, when all the ice is removed. Bound water is removed by heating under vacuum. The mode of heat transfer is similar to that of primary drying. Drying rate during secondary drying stage is much lower than that of primary stage and this is one of the contributing factors for longer drying time of freeze drying (Mellor 1978; Flink & Knudsen 1983; Liapis & Bruttini 1995).

3.7 Foam-mat freeze drying of egg white

Foam-mat drying of whole egg was studied by Rao et al., as early as 1987. At that time, it was only laboratory study and the progress in foam-mat drying after that was relatively minimal. Nevertheless the method has its own advantage, as the drying rate is higher than conventional methods. Reduced drying ensures savings in energy cost and overall production cost (Karim & Wai 1999; Falade et al. 2003). The quality of the dried product was also good.

Foam-mat freeze drying of egg white has not been tried before and hence there is limited information in the literature. But still it is possible to apply the same principles underlying conventional freeze drying. Due care should be taken in experiments and further data analysis to properly assess the potential of the method.

3.7.1 Effect of stabilizer on foam-mat freeze drying

Addition of stabilizer to egg white foam can play a major role in affecting foam-mat freeze drying in many ways. First the stabilizer helps to avoid drainage of liquid from foam during freezing thereby keeping foam structure intact. This is especially important in the case of foam-mat freeze drying to assess the effect of foaming on freeze drying process. If egg white without stabilizer is used during the freezing operation, the

structural collapse even before the onset of freezing can adversely affect the fundamental principle of foam-mat drying. Hence, it is important to add proper stabilizer in appropriate quantities to avoid this problem (Pugh 2001; Kampf et al. 2003; Foegeding et al. 2006).

3.8 Mathematical modelling

Mathematical models can be defined as "mathematical construct designed to study a particular real-world system or phenomenon" (Giordano et al. 1997). Modeling can be classified into theoretical, empirical and semi-theoretical based on the approach used to develop the model. Mathematical modeling comes under theoretical modelling. Theoretical models can be quite complex, and require lot of computing power to solve them. If properly constructed, the theoretical models can be more powerful and their results will be accurate. Theoretical models can also be used to explain the phenomena, whereas other two models cannot be used for this purpose (Bala 1997).

Freeze drying produces very good dehydrated product with good rehydration properties. But the cost of operation is one of the major inhibiting factors for widespread adaptation of this method. As developing prototype models also cost more, it is better to do simulation studies which can predict the results as well as its ability to describe the phenomena involved. Mathematical modelling is one of the available tools; if constructed well this method can give better results at lower costs. This method can also be used as primary tool for analyzing the conditions before constructing prototypes, which can greatly reduce the cost of research and development. Mathematical models have been developed for both steady state and unsteady state conditions. Unsteady state models are usually formulated by a set of partial differential equation. Models developed based on

partial differential equations have very complex solutions but they can better explain the drying process (Liapis & Bruttini 1995; Barbosa-Canovas & Vega-Mercado 1996; Bala 1997; Jafar & Farid 2003; Karel & Lund 2003).

Earlier drying models were based on pure mass transfer and the effect of heat transfer was completely neglected. Mass transfer mechanism was assumed to be either by capillary or diffusion. But lot of research has been done in this area, with more parameters and conditions. Many mathematical models have been proposed to describe drying (Karim & Hawlader 2005). Freeze drying involves simultaneous heat and mass transfer and this has to be taken into account when models are developed. However, the conditions governing heat and mass transfer are often simplified to model freeze drying to determine drying rate and diffusion coefficient. Complex models are necessary to better describe drying kinetics during freeze drying. But it would be a better approach to start with simple models and improve the model to better describe the process (Karel 1975; Flink & Knudsen 1983; P. Sheehan 1998).

3.8.1 Heat Transfer

In case of solid foods, heat transfer is usually modelled using Fourier's conduction equation. Most of the models can be solved analytically but they are often very complex, hence numerical solutions are widely used for solving heat transfer models (Wang & Sun 2003). Some researchers analyzed radiation heat transfer method for freeze drying. In this case, heat passes through the dry layer and is absorbed at sublimation interface. If radiation is a major source of heat supply, the freeze drying is heat transfer controlled and sublimation temperature becomes constant. Internal heat transfer resistance is much higher than mass transfer resistance. Quasi-steady state model is

widely used for modeling radiation heat transfer during freeze drying. This method ignores the effect of sensible heat on overall freeze drying. Another method is based on transient heat conduction equations, which takes into account both frozen and dried regions. Convection heat transfer is often neglected during freeze drying calculations, as vacuum present inside the drying chamber does not help this mode of heat supply (Arsen & Ma 1990; Litvin et al. 1998; Jafar & Farid 2003).

3.8.2 Mass Transfer

Diffusion models are widely used in describing the mass transfer mechanism. The popularity of the diffusion models can be widely attributed to their ease of formulation. In many situations, diffusion models give satisfactory results and can also serve as a first step towards developing more complex models. The complexity of the model can depend on many parameters like properties of the material being dried, drying method, drying conditions and drying time (Akpinar & Dincer 2005).

The mass transfer models are usually based on Fick's law (both first and second). Fick's first law is widely used for describing steady state diffusion. According to Fick's first law (Lienhard IV & Lienhard V 2005),

$$J = -D\frac{\partial \phi}{\partial x} \qquad \text{..... (3.1)}$$

Fick's second law is used to describe mass transfer during un-steady state diffusion (Lienhard IV & Lienhard V 2005),

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2} \qquad \text{..... (3.2)}$$

The diffusion coefficient of the material can be dependent on the temperature. This temperature dependence is found by applying the well-known Arrhenius-type equation (Lienhard IV & Lienhard V 2005),

$$D = D_0 e^{-\frac{E_A}{RT}} \qquad \text{..... (3.3)}$$

Simple diffusion models are also widely used for the calculation of mass transfer during freeze drying. Drying rate constant and diffusion coefficient can be obtained from the data and these values can be used in further calculations (Bala 1997).

3.8.3 Heat and mass transfer models

Many researchers have developed theoretical models to describe heat and mass transfer during freeze drying and they are widely available in the literature. Most of these theoretical models help to determine temperature profile, drying time and position and movement of ice front. The analytical and even numerical solutions for many of the theoretical models are often very complex. To reduce the complexity of the model some of the parameters involved like initial temperature, heating mode and direction (one-dimensional or multi dimensional) and interface temperature are often assumed or simplified or completely ignored (Flink & Knudsen 1983).

Karel (1975) developed one of the earliest and simple models to describe heat and mass transfer through dry layer in freeze drying of a solid material.

$$t = \frac{L^2 \rho m_s (X_0 - X_f)}{8Per(P_0 - P_{sat})} \qquad \text{..... (3.4)}$$

When, this model is compared with simultaneous heat and mass transfer theories, it is equivalent of the following model;

$$t = \frac{L^2 \rho m_s (X_0 - X_f)}{8 k_d (T_s - T_0)} \qquad \text{..... (3.5)}$$

Karel's model works well in most of the occasions and is widely used for freeze drying calculations.

Flink and Knudsen (1983) developed following model for freeze drying of slab with heating on both sides,

$$\frac{P_i - P_c}{-dW/dt} = \frac{LRi_s}{2k_c M_w V} + \frac{RTRi_s^2}{4D' M_w V}(1-W) \qquad \text{..... (3.6)}$$

Flink and Knudsen's model can be used for calculating diffusivity (D') of the material and external mass transfer coefficient (k_c), if we know the partial pressure inside the drying chamber and at the interface as well as the moisture loss during dehydration. The advantage of Flink and Knudsen's model over Karel's (1975) model (Eqn 3.4 & 3.5) is that it could be better used for freeze drying of sample between two plates where, conduction is the major mode of heat transfer.

Another model developed by Liapis and Sadikoglu (1997) could also be used in freeze drying calculation and is little more complex than the previous examples. The model tries to explain both heat and mass balances during freeze drying.

$$\frac{\partial T_I}{\partial t} = \alpha_{Ie}\left(\frac{\partial^2 T_I}{\partial x^2}\right) - \frac{C_{p_g}}{\rho_{Ie} C_{pIe}}\left(\frac{\partial (N_t T_I)}{\partial x}\right) + \frac{\Delta H_v \rho_I}{\rho_{Ie} C_{pIe}}\left(\frac{\partial C_{SW}}{\partial t}\right), \quad 0 \le x \le X \qquad \text{.... (3.7)}$$

$$\frac{\partial T_{II}}{\partial t} = \alpha_{II}\frac{\partial^2 T_{II}}{\partial x^2}, \quad X \le x \le L \qquad \text{..... (3.8)}$$

$$N_w = -D_{win,e}\frac{\partial C_{pw}}{\partial x} + \left(\frac{C_{pw}}{C_{pw} + C_{pin}}\right)N_t \qquad \text{..... (3.9)}$$

$$N_{in} = -D_{win,e}\frac{\partial C_{pin}}{\partial x} + \left(\frac{C_{pin}}{C_{pw} + C_{pin}}\right)N_t \quad \text{..... (3.10)}$$

$$N_t = v_p(C_{pw} + C_{pin}) \quad \text{..... (3.11)}$$

This model can be used for determining overall mass transfer by applying the boundary conditions; this model also helps to include the effect of radiation heat transfer.

Some of the key assumptions made by the researchers (Liapis & Bruttini 1995; Liapis & Sadikoglu 1997; Jafar & Farid 2003; Khlloufi et al. 2005) to develop mathematical model for freeze drying are,

i) The maximum permissible surface temperature (T_s) is reached instantaneously

ii) The surface temperature is maintained constantly by adjusting external heat output

iii) Sublimation occurs parallel to the surface at the interface

iv) At the interface the concentration water vapour and the ice are in equilibrium

v) Solid layer is semi-infinite

vi) Binary mixture of water vapour and inert gas pass through dried layer

vii) In the dried layer, the solid and the enclosed gas are in thermal equilibrium

viii) Partial pressure variation inside the drying chamber is negligible

ix) There is no heat loss; all the heat input is used for sublimation of water

x) The frozen region is homogenous with uniform thermal conductivity, specific heat and density, and

xi) The frozen layer has negligible amount of dissolved gases

Some of the assumptions are not realistic, for example the maximum permissible temperature (Ts) cannot be reached instantaneously. The presence of dissolved gases can affect the vacuum level in the drying chamber as well as heat transfer. Usually the effect of dissolved gas is not included in freeze drying calculations. Hence, the models developed using this assumptions can fail to predict properly under certain conditions. Nonetheless, the models developed based on these assumptions gave fairly acceptable results when compared to experimental, which is an important step in model development (Liapis & Bruttini 1995; Jafar & Farid 2003).

Numerical models have been developed recently with more detailed equations to improve the accuracy of prediction. The solutions for numerical models are simpler than analytical models and availability of computing power makes numerical model appealing for many practical applications (Wang & Sun 2003).

Heat transfer rate during freeze drying depends on many factors and they are, thickness of the material, initial and final moisture content, latent heat of sublimation, thermal conductivity of the frozen product and dry layer, dry layer permeability, partial pressure of water near the drying surface and maximum permissible surface temperature. Higher dry layer permeability improves the mass transfer. Reduced pressure can help in removal of vapour and enhance overall heat transfer. Some of these factors are either simplified or neglected for model development as mentioned earlier and including more parameters will result in much better and complex model (Karel & Lund 2003).

IV. OPTIMIZATION OF EGG WHITE FOAM STABILITY FOR FOAM-MAT FREEZE DRYING

4.1 Abstract

Egg white (albumen) is a rich source of protein and is widely used in confectionary industry for its wonderful foaming ability. Foam-mat freeze drying is one of the promising methods of drying, which tries to utilize the advantages of both freeze drying and foam-mat drying to produce better quality egg white powder. Preliminary experiments showed that the stability of foams made with egg white alone is not adequate for foam-mat freeze drying. Experiments were thus conducted using different stabilizers (Methyl cellulose, Propylene glycol alginate and Xanthan gum) to optimize foam stability. Bubble size distribution was determined using microscopy technique to understand foam structure. This paper will discuss about the effect of stabilizers on the stability of egg white foam and possible mechanisms involved. The results showed that Xanthan gum at 0.125% provide sufficient stability for freeze drying.

4.2 Introduction

Egg white or egg albumen is widely used in food processing industries especially in bakery industry due to its ability to form higher volume and to produce relatively stable foam. One of the advantages of using egg white in bakery industry is that it improves the ability of the product to trap the air inside, which gives the characteristic spongy texture of the product (Alleoni & Antunes 2004; Foegeding et al. 2006). The egg white foam is an important ingredient in the preparation of many bakery foods such as breads, cakes, meringues, soufflés etc.

Foam is a two phase system having a dispersed phase (usually air) and a continuous phase. Dispersed phase is larger than the continuous phase (German & Phillips 1994; Baniel et al. 1997). A typical foam structure is shown in the Figure 4.1. The wall of the bubble is called as lamella & the dispersed phase is surrounded by a plateau border.

Foams are highly fragile and delicate in nature. The high levels of surface energy at the air-water interface make them thermodynamically unstable. Volume profile of typical foam during and after formation is shown in the Figure 4.2. The stability of foam depends on the thickness and the strength of lamella. Usually surface acting agents like stabilizers are used for improving the strength of lamella to increase the stability of the foam. In case of polyhedric foams, the system is more dynamic than a dilute foam due to the presence of enormous amount of bubbles and their surface activity. This makes polyhedric foams (such as egg white foam) unstable. Quantifying the stability of foam will help us in selecting proper stabilizer. Stability tests are also considered as the first step in any foam related studies (Murray 2002; Alleoni & Antunes 2004; Foegeding et al. 2006).

Stability of egg white foam is becoming important for many food processing applications. Generally, the drainage of water or liquid phase from the foam is measured as the deterrent factor in destabilizing the foam. Hence, measuring the drainage of foam is one of the better methods for the determination of its stability. Other methods used for the determination of foam stability are measuring the foam height over a period of time and measuring the weight loss of foam over a period of time (German & Phillips 1994). Also optical methods were used to determine the structural stability of foam. This

method can also be used for determining the structural parameters like cell wall thickness and yield stress as well (Nekrasov et al. 2002).

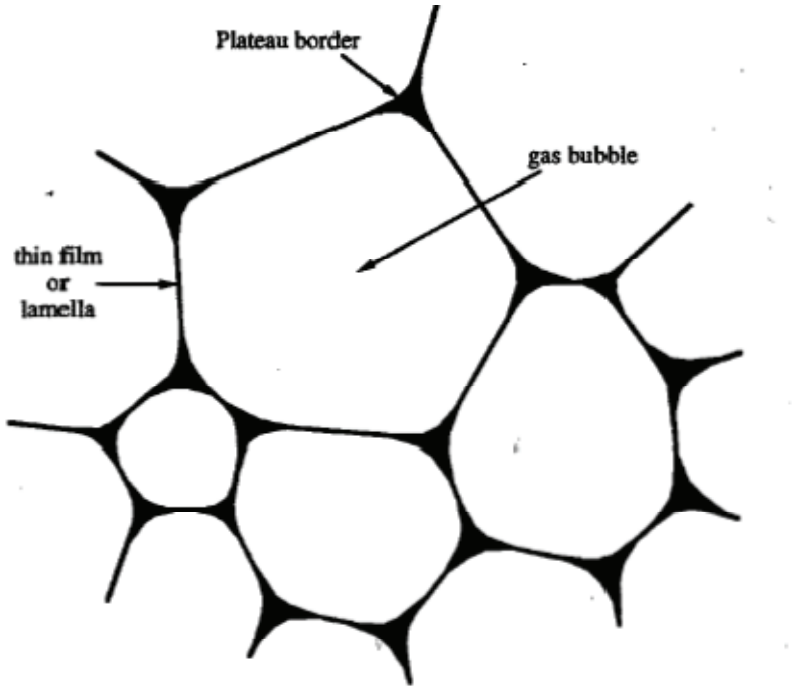

Figure 4.1 Structure of foam (Wilde & Clark 1996)

Often the natural stability of egg white foam may not be adequate to retain the structure over time; in those cases, the addition of food stabilizers are important to enhance the stability. Various types of stabilizers can be incorporated to egg white foam for this purpose. They are generally polysaccharide stabilizers such as Xanthan Gum (XG) and Propylene Glycol Alginate (PGA), which are widely used and they can be very effective even at lower concentrations.

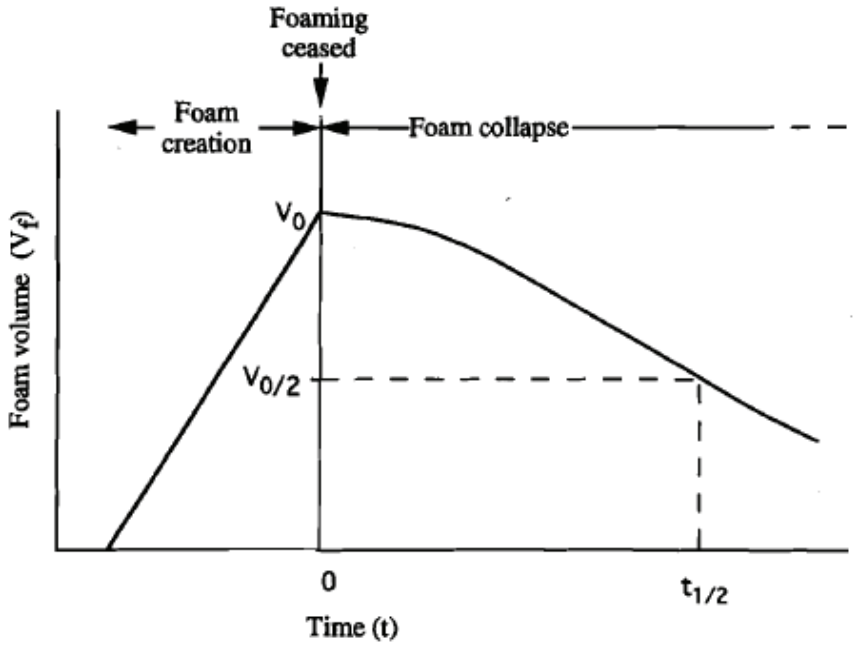

Figure 4.2 A typical foam volume profile during and after formation (Wilde & Clark 1996)

4.3 Objective

The main objective of this work is to optimize the stability of egg white foam for foam-mat freeze drying. The effect of adding different type of stabilizers on the stability of egg white foam will be studied to select the best stabilizer. The amount of stabilizer needed to achieve optimum stability will be determined. The bubble size distribution will be measured by microscopy.

4.4 Materials and Methods

4.4.1 Egg white or Egg albumen

The nutrient composition of egg is shown in Table 4.1. Egg white or egg albumen makes up to 58% of whole egg and is mostly composed of protein (Dry Basis). It has an

excellent foaming property, which has been exploited in many of the bakery and other type of food product industries. The foaming property of egg albumen can also be utilized for foam-mat freeze drying, which is one of the latest methods with the potential to reduce the processing time.

Table 4.1 Nutrient Composition of egg (per 100 g) (Britannica 2000)

	Whole egg	Egg white	Egg yolk
Energy, kcal	149	50	358
Water, g	75.33	87.81	48.81
Protein, g	12.49	10.52	16.76
Fat, g	10.02	0	30.87
Cholesterol, mg	425	--	1,281
Carbohydrate, g	1.22	1.03	1.78
Vitamin A, IU	635	--	1,945
Riboflavin, mg	0.508	0.452	0.639
Calcium, mg	49	6	137
Phosphorus, mg	178	13	488

4.4.2 Experimental Setup

Stability was assessed by drainage tests. A Buchner filter (90 mm), a graduated glass cylinder (250 ml) and a stand were used for the determination of foam drainage. The foam was placed into the Buchner filter (fixed on the stand) and the measuring cylinder was placed directly under the filter to collect the drainage from the foam by natural gravity. A digital timer was used to measure the time interval during the foam drainage period. The same set up was used for all the replications. The size and

configuration of the Buchner filter and measuring cylinder were maintained uniform throughout the experiment.

In order to determine the optimum stabilizer, the experimental design studied the following combinations: egg white foam without any stabilizers, egg white foam with Xanthan Gum (0.125%, 0.25%, 0.375% & 1% (w/w)), egg white foam with Propylene Glycol Alginate (0.25%, 0.5%, 0.75% & 1% (w/w)) and egg white foam with Methyl Cellulose (0.25%, 0.5%, 0.75% & 1% (w/w)). The stabilizers were chosen based on the work of various researchers reported in the literature (Katzbauer 1998; Karim & Wai 1999; Garcia-Ochoa et al. 2000; Kampf et al. 2003; Papalamprou et al. 2005). The concentration levels were chosen based on the preliminary experiments.

A 250 Watt kitchen blender (Black & Dekker, USA) with various speed settings was used to produce egg white foam. A fluorescence microscope (Olympus BX51, Carsen Group Inc., Ont., Canada) with UIS2 optics (to deliver bright images) was used for the microscopic determination of foam size distribution. A CCD digital camera attached to the microscope was used to take photographs having an area of 1030 mm x 1300 mm. Image Pro Plus (Mediacybernetics) software was used to count the number of bubbles, to determine their size, shape and distribution.

4.4.3 Experimental Procedure

4.4.3.1 Foam preparation

Commercially available liquid egg white (Simply Egg White© by Burnbrae Farms) was used for the experiment. Egg white was kept under refrigeration at 5° C until the experiment. Before starting the foaming experiment, the egg white was removed from

the refrigerator and kept outside to obtain equilibrium with ambient conditions (approximately 15 °C) to help foam formation.

A glass beaker was used as a container to form the foam. One hundred (100) ml of egg white was measured and added to the glass beaker. As per the experimental design, proper amount of stabilizers were measured (if stabilizer added) to have required final concentration (as explained previously). The kitchen blender with a speed of 4000 rpm (optimum speed was based on the preliminary experiments) was used for all the experiments. The stabilizers were added gradually during whipping of the egg white. The total whipping time was selected as 5 minutes.

4.4.3.2 Drainage measurement

The volume (V) of liquid collected in the graduated cylinder from the foam was measured every 5 minutes by directly reading on the graduated cylinder (ml) during the period of 120 minutes. Three replications were carried out for each experimental design and the average value was taken for analysis. The data was analysed by using Microsoft Excel© 2003 (Microsoft Inc., USA) and SigmaPlot package (Version 9.0, Systat Software Inc., Richmond, Calif., USA).

4.4.3.3 Bubble size distribution

As explained previously, microscopy was used to determine the bubble size distribution of the foam. The required amount of freshly formed foam (with 0.125% Xanthan Gum) was placed on a clean glass slide for microscopic examination. A cover slip was placed on the top of the foam carefully, since pressure should not be given to the sample while placing the cover slip to avoid deformation of the foam. A glass slide was placed under the microscope with a 4X bright optical lens, for viewing the foam. A CCD

camera attached to the microscope was used to take the photograph of the foam, which was later analysed using the Image Pro Plus software.

4.5 Results and Discussions

The comparison of foam drainage during the period of 120 min is shown in Figure 4.3. From the figure, it is observed that the addition of foam stabilizer plays a major role in the stability of egg white foam. In the case of egg white foam without stabilizer, the foam drainage rapidly increased. After 120 minutes, the drainage volume was 54 ml, which is almost 50 % reduction of the initial volume of the egg white foam used for this study.

Among the PGA concentrations used for the foam stability study, 0.25% PGA did not have much effect on stability and the drainage was almost similar to that of foam without stabilizer, but at higher concentrations it had a better effect in improving the stability. At 0.5%, the foam drainage was recorded as 23 and 39.5 ml after 60 and 120 minutes, respectively. Similarly at 0.75% and 1% PGA level, the foam drainage volumes recorded are 6.67 and 24.5, 4.33 and 8.83 ml, respectively after 60 and 120 minutes. It is clear from the drainage study with PGA that its effect on foam stability was higher at 1% concentration, when compared to 0.75% and 0.5% of PGA concentrations.

Methyl cellulose made the foam very sticky, which completely clogged the filter and prevented proper movement of the drained liquid from the funnel to the glass cylinder. Hence the data obtained from methyl cellulose was not used for further studies.

The foam drainage with 0.125% Xanthan Gum (XG) treated egg white sample showed that there was virtually no drainage (only 1 ml after 120 minutes). The lowest liquid drainage inferred that there is a good interaction between egg white and XG in

terms of stability (even after 120 minutes). A similar study on foam stability was reported by Kampf et al. (2003). Results on other XG concentrations are not shown since the stability at 0.125% was already excellent.

The bubble size distribution for egg white foam made with 0.125% XG is presented in the Figure 4.4. From the figure, it is clear that the maximum number of bubbles were in the size range of 30 – 40 μm diameter, which was followed by 20 – 30 and 10 – 20 μm diameter bubbles. Though the foam bubble sizes were in the range from 1 to 220 μm diameter, the maximum number of bubbles were in the lower size range (Figure 4.5); which is a highly useful factor with respect to increased surface area of the foam bubbles for the subsequent heat and mass transfer studies.

The effect of each stabilizer on the stability of egg white foam was statistically analyzed using Duncan analysis with the confidence level of 95% as shown in Table 4.2. From the analysis it is clear that Xanthan Gum at 0.125% had significantly higher effect on stabilizing the egg white foam, when compared to other stabilizers even at higher concentrations.

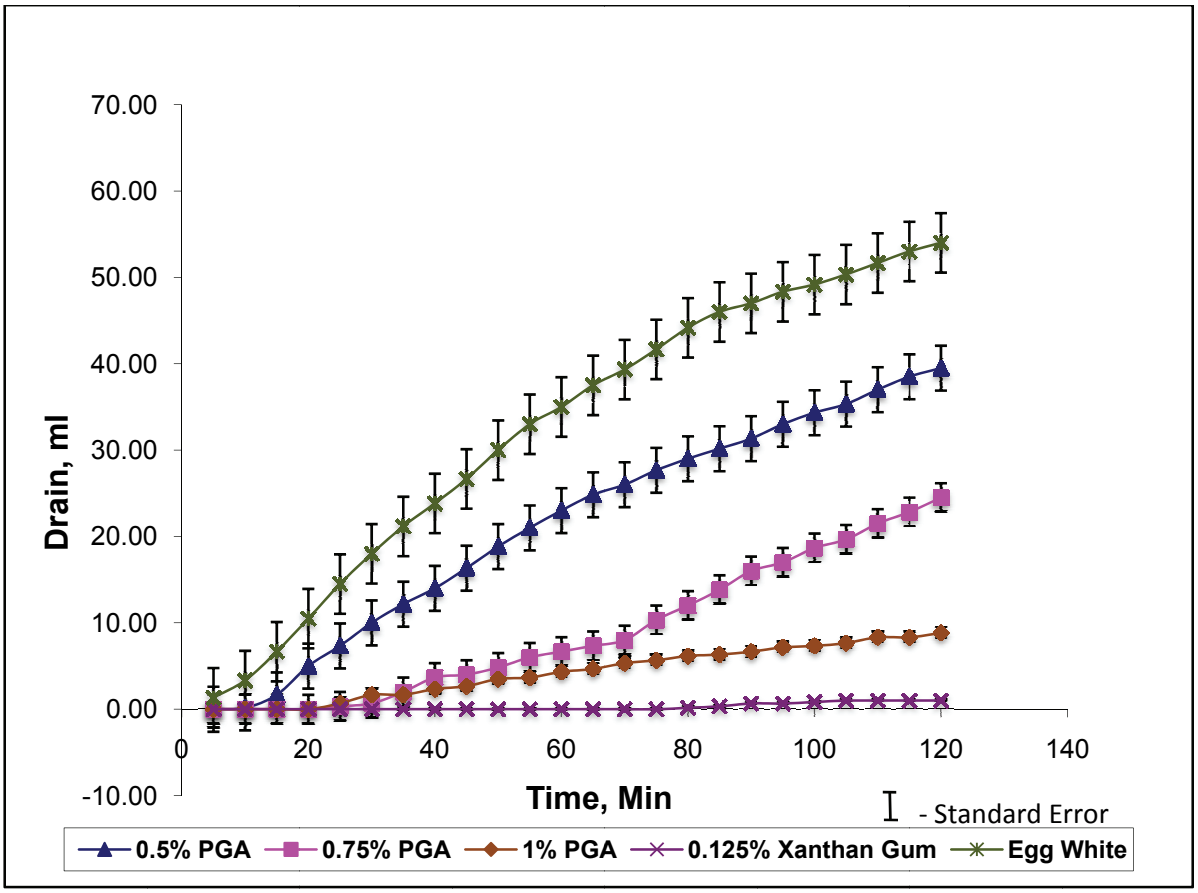

Fig 4.3 Comparison of drainage in egg white foam without stabilizer and with Propylene Glycol Alginate (0.5%, 0.75% & 1%) and Xanthan Gum (0.125 %)

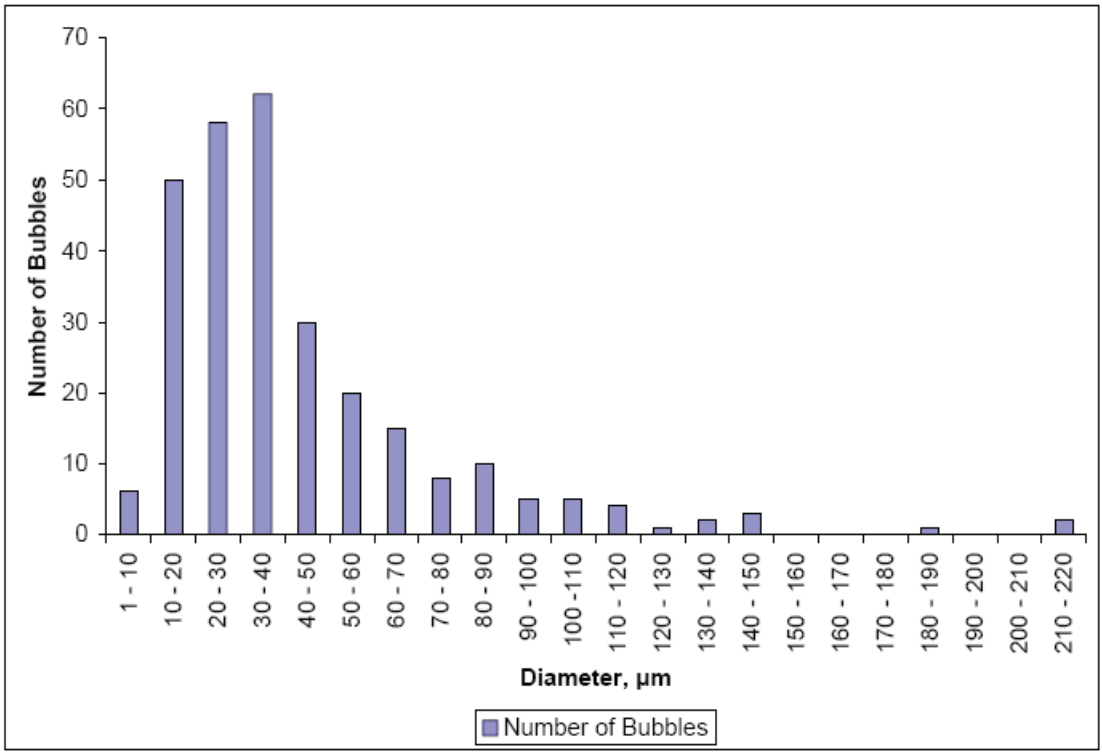

Fig 4.4 Bubble Size Distribution for Egg White foam with 0.125% Xanthan Gum

Table 4.2 Foam Stability for different stabilizers

Stabilizer	Concentration, %	Total Drain, ml	Mean
Xanthan Gum	0.125	1.00	0.118[a]
Propylene Glycol Alginate	1	8.83	4.292[b]
Propylene Glycol Alginate	0.75	24.50	9.160[c]
Propylene Glycol Alginate	0.5	39.50	21.507[d]
Egg White Without Stabilizer	0	54	25.958[e]

Duncan Groupings: Means with same letters are not significant

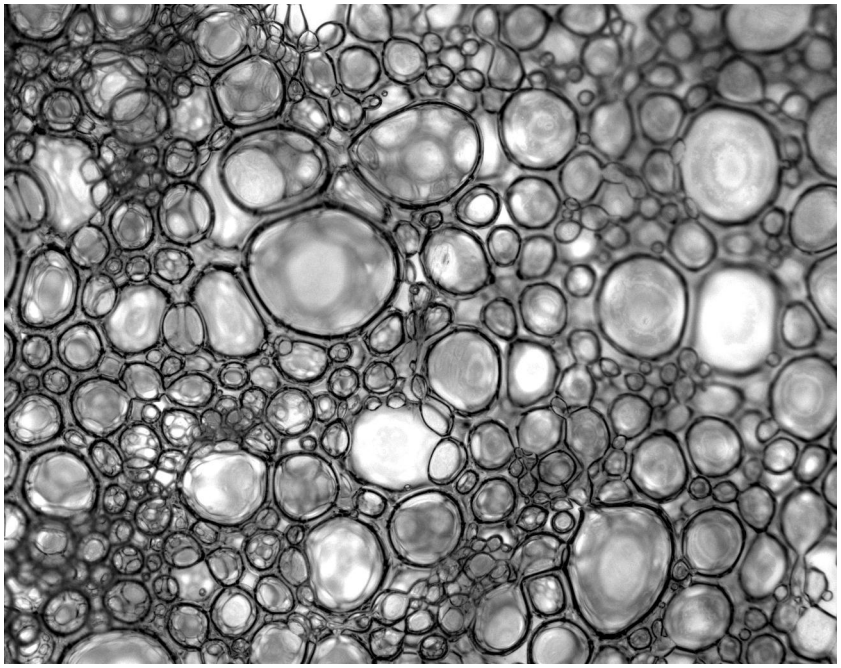

Fig 4.5 Egg white foam (with 0.125% Xanthan Gum) structure (5X Magnification)

4.6 Conclusion

Propylene Glycol Alginate and Xanthan Gum at different concentrations were used for optimizing the stability of egg white foam. Xanthan Gum produced highly stable egg white foam at very low concentration (0.125% w/w). The Duncan analysis also confirms the marked effect of Xanthan Gum over a period of time on the stability of egg white foam. Other stabilizers at higher concentrations were able to achieve reasonable stability, but much lower than the Xanthan Gum. Methyl cellulose could not be used as it clogged completely the filter and prevented the proper measurement. Hence Xanthan Gum at 0.125% (w/w), was chosen as stabilizer for foam-mat freeze drying of egg white.

4.7 References

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CONNECTING TEXT

The previous chapter dealt with the optimization of egg white foam, as the stability of the foam is expected to play a major role in overall freeze drying of egg white foam. The next chapter will describe the foam-mat freeze drying of egg white and the determination of drying time. The effect of stabilizer on freeze drying time of egg white foam and the change in mass transfer rate during drying are also discussed. Use of simple mathematical models for the prediction of drying time and its effectiveness is compared with actual data obtained in the experiments.

V. FOAM-MAT FREEZE DRYING OF EGG WHITE - MATHEMATICAL MODELING

5.1 Abstract

Foam-mat freeze drying is one of the promising methods of drying, which utilizes advantages of both freeze drying and foam-mat drying. Egg white with its excellent foaming properties makes a suitable candidate for foam-mat freeze drying. Experiments were conducted to study foam-mat freeze drying of egg white, in an effort to determine the suitability of this method. Xanthan Gum (XG) at 0.125 % concentration was used as stabilizer for foaming. The results showed that the addition of Xanthan Gum during foaming has a positive impact in reducing the total drying time and also produces excellent quality egg white powder. The addition of stabilizer also plays an important role in improving drying. Simple models were applied for determining drying time and diffusion coefficients during freeze drying.

5.2 Introduction

5.2.1 Freeze drying

Freeze drying is one dehydration method, which can produce high quality dried products. This method takes advantage of triple point of water. Triple point is a state in which substances coexists in different states such as solid, liquid and vapour and remain in thermodynamic equilibrium. Water has triple point at 0.01 °C and 611.73 Pa. Below triple point of water the ice can be directly sublimated into water vapour. This method of moisture removal gives many advantages over conventional methods (Geankoplis 1993).

Freeze drying has several advantages over conventional drying methods like absence of air during drying, which reduces the risk of oxidation, preservation of flavour and volatile components, absence of movement of solvent during drying and excellent re-hydration properties. But the cost of operation is high as the drying rate is usually low, especially during secondary drying stage. Application of vacuum during drying increases in addition to the total drying cost. Hence, freeze drying has conventionally been used only for high quality and high value commercial products (Liapis & Bruttini 1995; Liapis & Sadikoglu 1997; Vega-Mercado et al. 2001; Jafar & Farid 2003).

5.2.2 Foam-mat drying

In foam-mat drying the product to be dried is converted into foam before drying. This gives an advantage of increasing the total surface area available for drying thereby improving mass transfer and drying rate as well. Another advantage with this method is that the drying temperature can be lower than that of conventional drying methods and this helps to reduce the loss of flavour and volatile components. Foam-mat drying was studied by Rao et al., in 1987 for dehydration of whole egg. In their work they compared freeze drying of whole eggs to foam-mat drying and concluded that foam-mat drying produces higher quality dried product. Foam-mat drying was also tried for drying of cowpea (Falade et al. 2003), star fruit (Karim & Wai 1999) and mango (Jaya & Das 2004).

5.2.3 Modeling

Modeling can be classified into theoretical, empirical and semi-theoretical based on the approach used to develop the model. Mathematical modeling comes under theoretical modelling. Theoretical models can be quite complex, and require lot of

computing power to solve them. If properly constructed, the theoretical models can be more powerful and predictions can be done with accurate results. Theoretical models can also be used to explain the phenomena, whereas other two models cannot be used for this purpose (Bala 1997).

Heat and mass transfer models have been widely used in many of the drying applications to determine drying parameters like drying time, heat transfer rate, mass transfer rate and diffusion coefficient. Many models have been developed for drying and (some of them specifically for freeze drying) and are widely available in the literature (Karel 1975; Mellor 1978; Flink & Knudsen 1983; Sheehan & Liapis 1998; Fellows 2000; Jafar & Farid 2003; Karel & Lund 2003; Khlloufi et al. 2005).

5.3 Objective

Both freeze drying and foam-mat drying methods could be combined to achieve faster freeze drying, by utilizing increased surface (mass transfer) area made available by foaming. But this hypothesis should be tested to prove its validity. Hence, the main objective of this work is to determine the suitability of foam-mat freeze drying for egg white dehydration and to estimate the drying time. Simple heat and mass transfer models were also applied to determine drying time and drying rate during foam-mat freeze drying.

5.4 Materials and methods

5.4.1 Experimental procedure

5.4.1.1 Foam preparation

Commercially available Liquid egg white (Simply Egg White© by Burnbrae Farms) was used for the experiment. Egg white was kept under refrigeration (5 °C) until the next step of experiment (not more than 48 hours). If the temperature of the egg white is lower than the ambient conditions it can adversely affect the foam formation; hence, before the experiment the egg white was removed from the refrigerator and kept outside to let the temperature to come into equilibrium with the ambient conditions.

A graduated glass beaker was used as a container to make the egg white foam. One hundred ml of egg white was measured and added to the glass beaker. Xanthan Gum (XG) (MP Biomedicals, Inc, France) at 0.125% concentration was used as a stabilizer. A 250 Watt, kitchen blender (Black & Dekker, Black & Dekker Co, USA) with various speed adjustments was used for making foam. The XG of 0.125% concentration was added gradually during the whipping for the stability of egg white foam. The total whipping time was 5 minutes. Egg white without stabilizer was used as control to compare the effect of XG on foam-mat freeze drying.

5.4.1.2 Freezing

Twenty five grams of foam was placed in a cylindrical glass beaker (Fisherbrand PLAIN 12 550D) of 25 x 75 mm dimension. The thickness of the sample was 20 mm and the volume of the sample was 119.5 x 10^3 mm^3. Before freezing the sample at -40°C, thermocouples were placed in the middle of the sample to measure the center temperature

during freeze drying. Freezing was done in a medical freezer (Sanyo MDF – 234, Japan). The sample was allowed to freeze completely for 24 hours.

5.4.1.3 Drying

The frozen egg white foam sample was dried in a Unitop 400 L (Virtis, NY) freeze drier. The temperature of the heating plate was reduced to -40 °C before placing the sample inside. The frozen samples were then placed inside the drying chamber of the freeze dryer and the thermocouples were connected to a digital data logger (21X Micrologger, Cambell Scientific Inc., UT) for automated temperature measurement during drying. After the samples were placed inside the drying chamber the vacuum pump was turned on to reduce the total pressure. Once the pressure inside the drying chamber is reduced, the heating system (1 °C/min) is turned on to increase the heating plate temperature to 20 °C.

The drying was done at 2, 4, 6, 8… and 24 hr durations. For each time, the same procedure mentioned above was followed. Five replications were done for each experimental conditions. After completing the drying process, the vacuum inside the drying chamber was released slowly and then the samples were transferred to desiccators for attaining equilibrium. The final mass of the foam-mat freeze dried sample was measured by using an electronic balance (Mettler Toledo Balance, PB 1502, ± 0.01g, Switzerland).

Egg white without stabilizer and foaming (25 g) were freeze dried to compare their drying rate and the effect of foaming and stabilizer on the drying time.

5.4.1.4 Determination of Moisture content

The dried mass of the sample was determined in a vacuum oven in order to calculate the moisture content. The final sample was placed inside the oven and was dried at 50 °C to attain bone dry condition. P_2O_5 was used as desiccator inside the vacuum oven. From the final dried mass and the freeze dried mass of the sample, the moisture content was calculated. Initial moisture content of the egg white was also determined using vacuum oven. Moisture contents on wet basis and dry basis were determined (Eqn 5.1 & 5.2) for all the replicated freeze dried samples (Bala 1997).

$$X_{(wb)} = \frac{m_o - m_f}{m_o} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.1)$$

$$X_{(db)} = \frac{m_o - m_f}{m_f} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.2)$$

Moisture ratio (MR) was calculated by Eqn (5.3) (moisture content values were on wet basis) to determine the water loss during freeze drying (Bala 1997).

$$\text{Moisture Ratio}\,(MR) = \frac{X}{X_0} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.3)$$

Drying rate is one of the important parameter, which helps us to understand the drying characteristics of a material. It is a moisture loss over a period of time and is calculated by the equation (Bala 1997),

$$\text{Drying Rate} = \frac{\Delta X}{\Delta t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.4)$$

5.5 Freeze-drying models

Karel (1975) made the following assumptions when describing his model for freeze-drying:

i) The maximum permissible surface temperature (T_s) is reached instantaneously

ii) The surface temperature is maintained constantly by adjusting external heat output

iii) Sublimation occurs parallel to the surface at the interface

iv) At the interface the concentration water vapour and the ice are in equilibrium

v) Solid layer is semi-infinite

vi) Binary mixture of water vapour and inert gas pass through dried layer

vii) In the dried layer, the solid and the enclosed gas are in thermal equilibrium

viii) Partial pressure variation inside the drying chamber is negligible

ix) There is no heat loss or accumulation; all the heat input is used for sublimation of water

x) The frozen region is homogenous with uniform thermal conductivity, specific heat and density

xi) The frozen layer has negligible amount of dissolved gases and

xii) Only primary drying stage was considered for the model development

In this model, heat and mass transfer is supposed to take place in dry layer but in opposite directions to simplify the model development. In this scenario heat can be supplied by conduction alone or in combination with radiation. Convection heat transfer is often neglected as it has very little effect on freeze drying due to vacuum inside the drying chamber. Ice front is assumed to recede uniformly on both sides toward the

middle layer during drying. The sample has slab geometry and only half thickness (t) is used for calculations.

Karel's (1975) model can be expressed as:

$$t = \frac{L^2 \rho m_s (X_0 - X_f)}{8 k_d (T_s - T_0)} \qquad \text{..... (5.5)}$$

In this model, most parameters such as product thickness (L), product density (ρ), moisture content and temperatures are available from experimental data. On the other hand, thermal conductivity of the dry layer (k_d) is difficult to measure at low values. In our case, thermal conductivity was determined by fitting the model to experimental data. The average thermal conductivity value was used for drying time predictions.

Moisture content X (kg moisture/kg dry matter) was plotted against time t (h) to prepare drying curves. Dimensionless water content expressed in an exponential form was used for fitting the experimental data:

$$\frac{X - X_e}{X_0 - X_e} = e^{-Kt} \qquad \text{..... (5.6)}$$

For most of the drying and moisture content calculations Eqn (5.6) is simplified, as equilibrium moisture content has negligible effect. Simplified Eqn (5.7) is used for calculating drying constant.

$$\frac{X}{X_0} = e^{-Kt} \qquad \text{..... (5.7)}$$

Where, K is known as drying constant. The drying constant is important in understanding the drying behaviour of the product. It decreases during drying and is similar to that of diffusion coefficient.

On the other hand, Fick's second law for diffusion (Eqn 5.8) was also used for determining the diffusion coefficient during drying:

$$\frac{X}{X_0} = Ae^{\left(\frac{-Deff*t}{4L^2}\right)} \qquad \text{..... (5.8)}$$

5.6 Results and Discussions

Temperature is one of the important parameters during freeze drying. The center temperature of frozen egg white foam was measured every 5 minutes during freeze drying. The average temperature variation at the center is shown in Fig 5.1. The initial drop in temperature is due to the time required to create vacuum inside the drying chamber during that period heat is not supplied for drying. The outside ambient temperature remained fairly constant during the process, which is shown in the graph to appreciate the variation in egg white foam during freeze drying.

For comparison, egg white without foaming having the same foam volume was freeze dried and the results are shown in the Fig 5.2. It is obvious from the drying curve that the moisture reduction was lower due to higher initial mass of the sample and it took nearly 15 h to remove 50% of ice as compared to only 6 h with foamed sample. Egg white without foaming having the same initial mass of egg white foam was also freeze dried and the results are also shown in Fig 5.2. The drying trend was almost similar to that of egg white foam.

Figure 5.3 shows the decrease in moisture content as a function of time for foams made with and without 0.125% Xanthan Gum. The moisture reduction was rapid during the initial stage of drying up to 6 h and then the moisture reduction slowed down and attained almost constant for the 20 to 24 hour period. From the graph it is also observed

that the time taken for drying of egg white foam with XG and without XG from the initial moisture content of about 88% (WB) to final moisture content of 7.74 and 8.47% was found to be 24 hours.

The drying rate curve for the egg white foam with 0.125% XG and without XG is shown in Fig 5.4. The drying rate of egg white foam with 0.125% XG and without XG was found to be 1.59 g/h and 1.19 g/h, respectively during the initial stage of drying. The drying rate during final stage of drying was found to be 0.35 g/h and 0.32 g/h for egg white foam with 0.125% XG and egg white foam without XG, respectively. Although the difference in drying rate between egg white foam with 0.125% XG and egg white foam without XG wasn't really high, the slight variation in the drying rate could be attributed to the presence of XG, which prevents collapse during freezing.

The drying rate of both, egg white foam with 0.125% XG and without XG was higher during the initial stage of drying because of the increased surface area due to foaming; which helped in faster removal of moisture from the sample. Obviously, the heat transfer must also be higher during the initial stage, due to foamed surface with higher moisture content. The drying rate was lower at the end of drying due to reduced moisture content of the egg white sample. Also as expected the drying rate of XG treated sample was slightly higher than that of the sample without XG due to the stabilized foamed surface during drying.

The drying rate vs. moisture content of the egg white foam with 0.125% XG and without XG (Fig 5.4) showed that the drying was mostly in falling rate period. This was mainly due to the higher moisture migration from the surface as drying proceeded.

The diffusion coefficients were obtained from the Eqn 5.8 by plotting the moisture content data *ln* (moisture ratio) *vs*. drying time for egg white foam with 0.125 % Xanthan Gum and egg white foam without Xanthan Gum as shown in Figures 5.5 and 5.6. Egg white foam with 0.125 % Xanthan gum had three diffusion coefficients (2.677×10^{-8} m^2/s, 5.962×10^{-8} m^2/s and 1.247×10^{-7} m^2/s) with an average diffusion coefficient of 7.036×10^{-8} m^2/s. The R^2 values were 0.9367, 0.9943 and 0.9641 respectively (Fig 5.4). But egg white foam without Xanthan Gum had only two diffusion coefficients (2.413×10^{-8} m^2/s and 3.781×10^{-8} m^2/s) with an average coefficient of 3.097×10^{-8} m^2/s and the R^2 values were 0.976 and 0.991 respectively (Fig 5.6). Higher diffusion rate during freeze drying allows better mass transfer and it is clear from Figure 5.5 that egg white foam stabilized with XG had better mass transfer than foam sample without XG during drying. The presence of more than one diffusion coefficient could be attributed to the fact that during initial stages of drying the resistance for mass transfer could be higher and gradual formation of porous structure enables improved mass transfer. This is evident from the diffusion coefficient values obtained from the experiment. When secondary drying stage is reached the diffusion coefficient value is reduced as this stage of drying involves with the removal of bound water.

The results obtained from freeze drying of foam with 0.125 % Xanthan Gum was fitted with Karel's model (Eqn 5.5). The thermal conductivity (k_d) was obtained (0.0781 kW/mK) as described earlier. Foam density (ρ) was measured during foam making and was found to be 226.47 kg/m^3. Latent heat of sublimation (2840 kJ/kg) was taken from the literature (Flink & Knudsen 1983; Liapis & Bruttini 1995). Same model was used for predicting the drying time and the result is shown in the Figure 5.7. The model was fairly

accurate in predicting the foam freeze drying time of egg white foam. The accuracy of the prediction of drying time becomes low when freeze drying enters secondary drying stage as it is apparent from the Figure 5.7. The model does not account for the radiation heat transfer and that could affect the prediction of the model. The thickness of the sample also can play a role in determining the accuracy of the sample as the temperature of the frozen layer depends on it.

The diffusion models developed for mass transfer based on fick's second law of diffusion was more accurate than heat transfer model. R^2 values obtained from the graph are also indicative of the conclusion. In the case of egg white foam with XG, there were three distinct drying stages, where as egg white foam without XG had only two distinct drying stages (Fig 5.5 & 5.6). In the case of heat transfer model number of parameters like radiation heat transfer, variable ice front movement, and constant heat transfer rate throughout drying could have affected the prediction. Some of the unrealistic assumptions like instantaneous reach of maximum surface temperature could greatly affect the performance of the model.

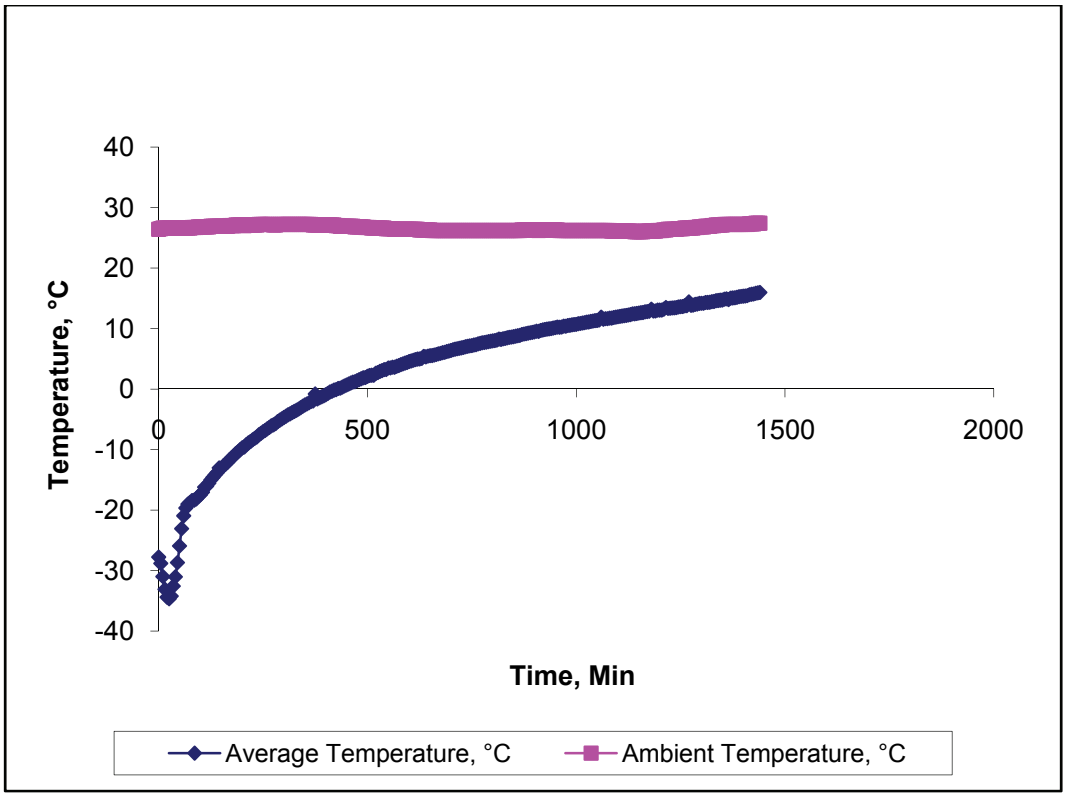

Figure 5.1 Center temperature variations during freeze drying of egg white foam with 0.125% Xanthan Gum – 24 h drying

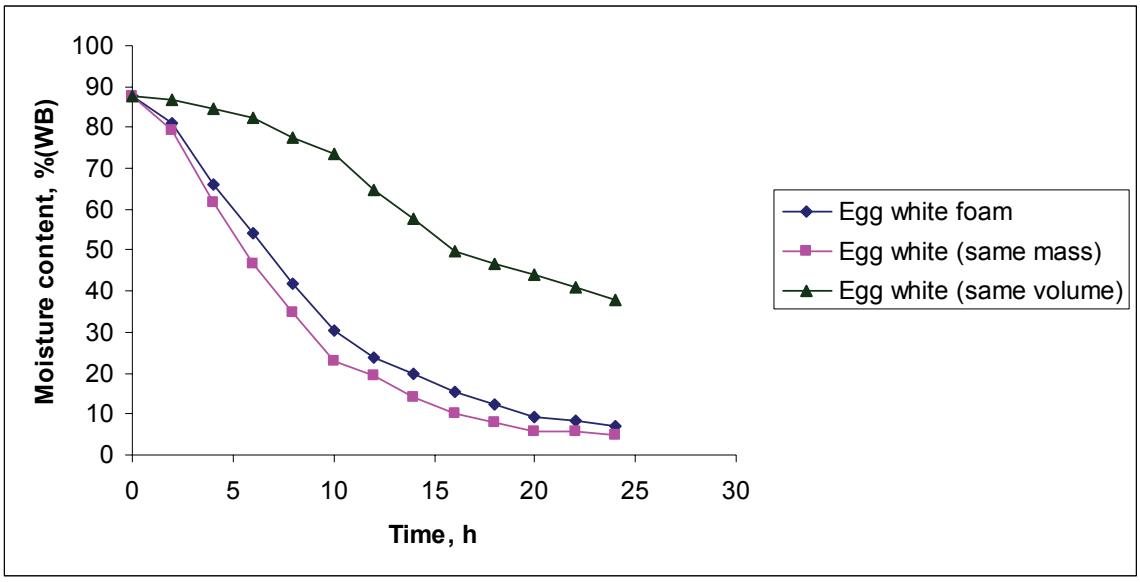

Figure 5.2 Comparison of freeze drying of egg white and egg white foam (all with 0.125% Xanthan Gum)

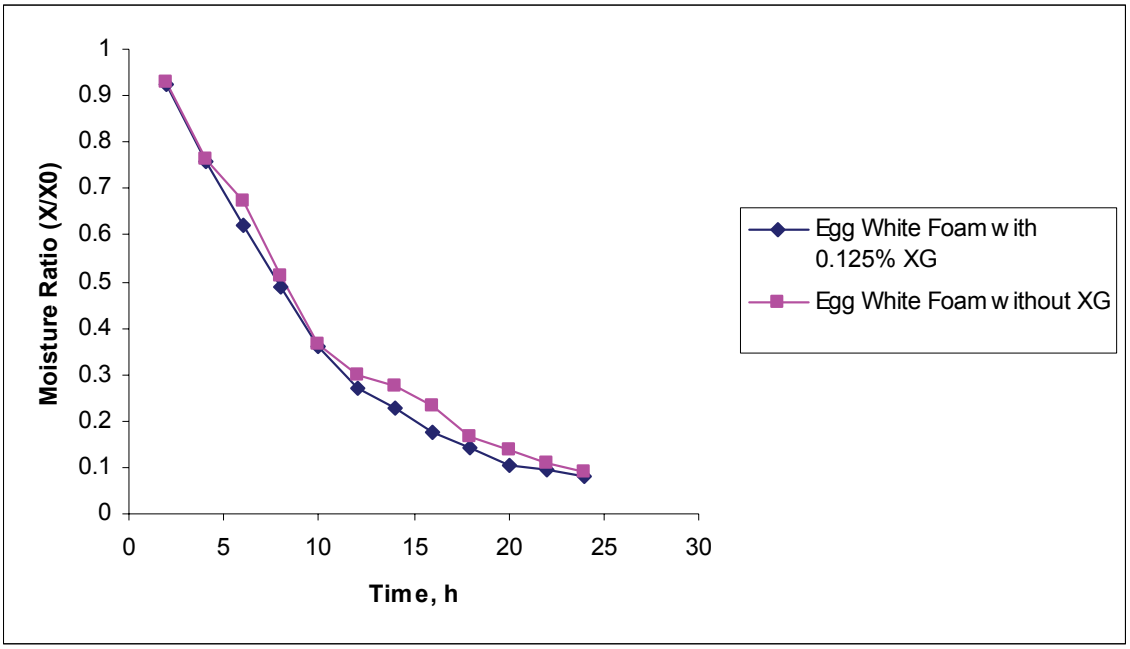

Figure 5.3 Foam-mat freeze drying of egg white with 0.125% Xanthan Gum & Egg White without Xanthan Gum – 24 h drying

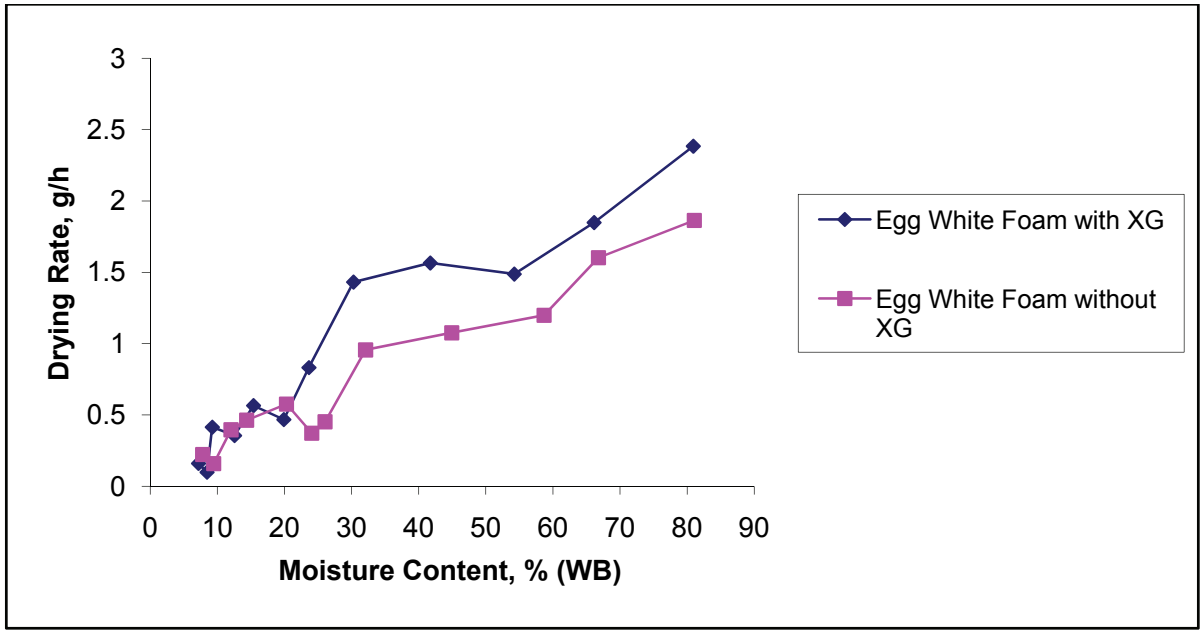

Figure 5.4 Comparison of drying rate vs. moisture content for foam-mat freeze drying of egg white foam with 0.125% XG and egg white foam without XG – 24 h drying

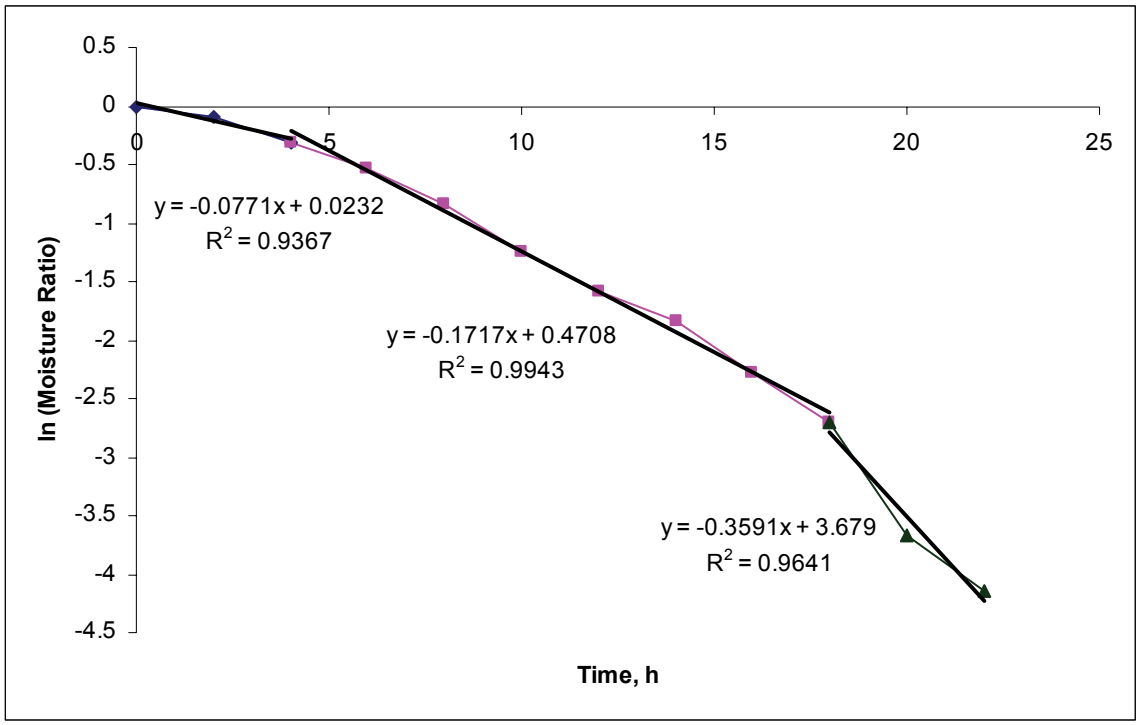

Figure 5.5 Moisture diffusion for foam-mat freeze drying of egg white foam with 0.125% XG – 24 h drying

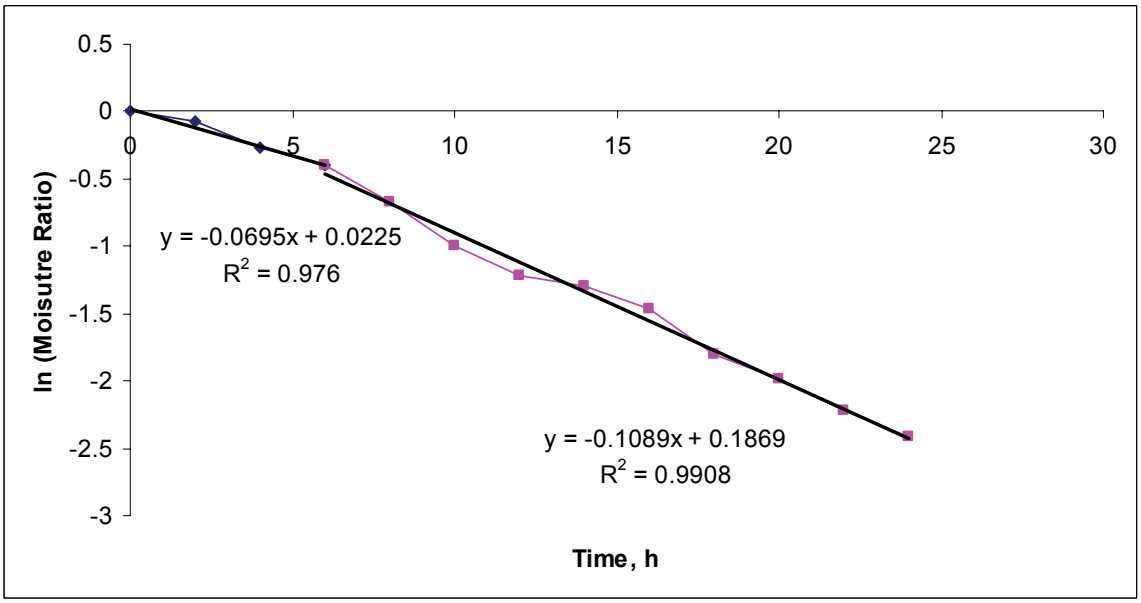

Figure 5.6 Moisture diffusion for foam-mat freeze drying of egg white without XG – 24 h drying

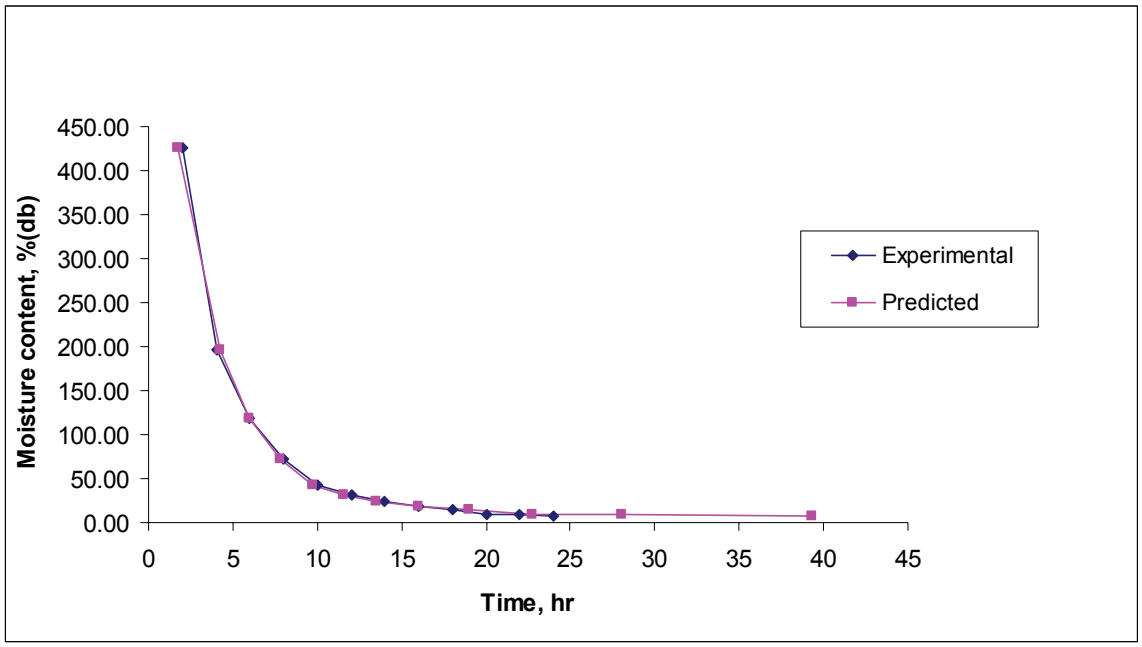

Figure 5.7 Drying time predictions for foam-mat freeze drying of egg white with 0.125 % Xanthan Gum – 24 h drying

5.6 Conclusion

The use of Karel's heat transfer model was appropriate and fairly accurate in predicting the drying time. But the thermal conductivity was determined from the experimental data and not determined separately. Determining the thermal conductivity of egg white foam could help a better understanding of the phenomena as well as the prediction of drying time. The diffusion models were more accurate for determining mass transfer rate and diffusion coefficient. The drying rate and moisture diffusion were higher with XG treated than without XG treated egg white foam.

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VI. GENERAL SUMMARY AND CONCLUSIONS

Foam-mat freeze drying of egg white has two distinct stages i) foam preparation and ii) freeze drying. Stability of foam is important to achieve better results and hence proper foam preparation is important. As the natural stability of egg white foam isn't good enough for foam-mat freeze drying, experiments were conducted to choose good stabilizer. In the experiment Xanthan Gum produced highly stable egg white foam at very low concentration (0.125% w/w). There was only insignificant amount of drainage from the foam during the experimental period of two hours. Duncan analysis also confirms the marked effect of Xanthan Gum over a period of time on the stability of egg white foam. Other stabilizers at higher concentrations were able to achieve reasonable stability but much lower than the Xanthan Gum. Methyl cellulose could not be used as it completely clogged the filter and prevented the proper measurement.

Foam-mat freeze drying experiments were carried out for egg white foam with Xanthan Gum and without Xanthan Gum. The initial moisture content of 88% (WB) was reduced to 7.74 and 8.47% (WB) for samples with Xanthan Gum and without Xanthan Gum respectively after 24 hours of drying. The use of Karel's heat transfer model was appropriate and fairly accurate in predicting the drying time. The thermal conductivity used in the model was determined from the experimental data and this could possibly influence the predictions of drying time. The diffusion models were more accurate for determining mass transfer rate and diffusion coefficient. The drying rate and moisture diffusion were higher with Xanthan Gum treated egg white foam than the sample without Xanthan Gum.

VII. RECOMMENDATIONS

This present study focuses mainly on the effect of foaming on freeze drying of egg white. The changes in nutritional quality attributes weren't measured and it is possible to conduct further research in this area to understand the changes and further validate the effectiveness of foam-mat freeze drying. In terms of heat transfer studies it was assumed that the effect of convective and radiation heat transfer were negligible and further studies could help us in better understanding this phenomena.

Heat and mass transfer were assumed to take place in wet and dry layers respectively. Other modes of heat and mass transfer on both wet layer or both on dry layers can be studied and models could be developed to improve the prediction of drying time further.

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