Experimental Analysis of Freeze Drying and Estimating the Transient Moisture Contents of Food Products

V. P. Chandramohan

Abstract Freeze drying is an advanced dehydration technology with many advantages over other traditional drying methods. The present work deals with development of an experimental model for freeze drying. The sample products used were skimmed milk and egg white. Experiments were performed with skimmed milk and egg white to estimate the transient moisture content. The experiments were performed with a laboratory lyophilizer setup and deep freezing was performed using a domestic refrigerator. The milk lost its 50% mass during the first 2.5 h freeze-drying process. It took 12 h to reach its solid powdered state. The egg white lost its mass very vigorously in the first 6 h of drying, and after that, a constant drying rate was noticed. The constant drying time continued up to 10 h. The egg white reached its solid state at 10 h. The obtained results were compared with existing numerical study, and a reasonable match was observed.

Keywords Freeze drying · Skimmed milk · Egg white · Lyophilizer · Transient moisture content

1 Introduction

Freeze drying is a hygienic process of dehydration which is used to protect food, medicines and biological applications. During the freeze-drying process, the water content in the material frozen and thereafter a high vacuum is applied on the product. Therefore, the frozen ice is sublimed to vapour directly without reaching the liquid state and hence the product is dried. Though it is an expensive process, the dried product can be saved for years without any action of micro-organisms through perfect air tight package. Whenever this freeze-dried product is used, enough water is added; therefore, the food regain its original aroma, flavour and colour [1, 2].

V. P. Chandramohan (✉)
Mechanical Engineering Department, National Institute of Technology Warangal, Warangal, Telangana 506004, India
e-mail: vpcm80@nitw.ac.in

V. Edwin Geo and F. Aloui (eds.), *Energy and Exergy for Sustainable and Clean Environment, Volume 2*, Green Energy and Technology,
https://doi.org/10.1007/978-981-16-8274-2_36

Considerable numbers of researches were made on freeze drying though both experiments and numerical estimations. Toei et al. [3] conducted freeze-drying experiments with a building material and found that a sublimation layer was formed during drying which was dividing the dried and frozen layer. The drying rate was low in the dried region as this region's thermal conductivity is low comparatively the frozen region. The stability criterion of the sublimation front was explained by the concept of zone sublimation. This experimental analysis found that the plane sublimation front was unstable, and it was broken into several zone sublimation regions.

Another study on the freeze-drying process used a sorption-sublimation model [4]. During the low pressure drying, the shortest drying time was estimated. Also, it was estimated that for small size samples, the bound water was more than the free moisture existing in the product. Also, it was proved that continuous freeze drying during the secondary drying led to undesirable effect in the solid food product.

A parameter called 'collapse phenomenon' was analysed by Pikal and Shah [5] though their experiments on moxalactam di-sodium with 12% mannitol. At high chamber temperature, the sublimation happens quickly, but during overheating, there was a loss of pore structure and it was called as a 'collapse phenomenon' which deteriorates the product quality. The product temperature depends on the chamber temperature and the pressure applied in the chamber and it could not be controlled directly during the drying process. In practice, trial-and-error experimental approach is used to find the suitable chamber temperature and pressure [6].

There is a detailed study on the effects of glass transition temperature that is one of the most important parameter which is responsible for the deterioration mechanism. It also determines the stability of the food product [7]. Glass transition temperature is the temperature at which the amorphous system changes to rubbery state from the glassy state. Glass transition temperature was experimentally determined for different products by variation of some thermodynamic or dielectric properties as a function of temperature. It also determined the quality of the food product. An easy approach to the glass transition phenomenon was presented by Genin and Rene [8] explaining its influence to different food products and reviewed several methods to determine it experimentally.

Time-scale modelling has been applied by Quiroga et al. [9] on freeze-drying process which is capable of describing freeze drying at the time scales. The model has been solved by finite element method. This model constitutes the core of the proposed optimal control approach, which defines the operation conditions for minimizing freeze–drying cycle time. A mathematical model was developed by Sadikoglu and Liapis [10] to describe quantitatively the dynamic behaviour of freeze-drying stages of pharmaceuticals in trays. The theoretical approaches were based on classical mass and heat transfer equations and simulated freeze-drying processes for the industry. Finite element analysis in two dimensional axisymmetric space has been considered by Mascarenhas et al. [11]. This model calculated the variation of partial pressure of water vapour, the temperature and the concentration of sorbed water. Lagarangian–Eulerian method was used to model the sublimation front of freeze-drying process which is the surface which separates the frozen and dried region. The developed finite element practice provided valuable information on primary and secondary drying stages.

Trelea et al. [12] developed a software tool for interactive selection of operating condition for freeze-drying process in order to maximize the efficiency in terms of productivity and product quality (obtaining of the highest quality in the shortest cycle time), and it was found that the product temperature was the most determinant one. The model was validated in a wide range of operating conditions: −25 to + 25 °C shelf temperature and 10–34 Pa chamber pressure. Hammami and Rene [13] worked on the production of high-quality freeze-dried strawberry pieces by the response surface method which is a quadratic model. This method was used to predict optimal solution from the fitting surfaces obtained from trial experiments. It is found that the processing conditions have an influence on both the quality of the strawberries and freeze-drying time. The freezing rate has no significant effect on the product quality or the freeze-drying time.

Few works are available on numerical solution of freeze drying as the complexity of governing equations is high. The proper handling of the product temperature is very important as it allows the maintenance of product quality and also reducing the process cycle time. Different boundary conditions were used by mathematical models [10, 14], where a product is set in chamber and sublimation is done by heating from the top with heating by radiation and by receiving conductive heat from the bottom of the chamber. There were other heating options available like microwave heating [15, 16] in which internal heat generation was considered. A mathematical model of vacuum freeze drying of random solids at microwave heating was explained by Nastaj and Witkiewicz [16]. Even for materials having considerable porosity, primary drying was not sufficient to remove entire moisture content. Secondary drying was necessary to remove the remaining residual moisture (more than 7%) after primary drying stage.

There were not many detailed studies on freeze drying experimentally and numerically as both ways have their own practical complexities. The specific results and its explanations were not observed to come out with definite conclusions. There were few studies on experimental analysis on freeze drying [17–19]. The transient mass transfer data is not found in any literature.

Hence, the main objectives of the present work are as follows: (i) to develop an experimental setup for freeze drying, (ii) perform experiments with the food products such as milk and egg white and (iii) to estimate the drying time and the moisture content of the products from the experiments.

2 Methodology

The experimental setup, selection of materials, sample preparations and experimental procedures are mentioned in this section.

2.1 Selection of Materials

The experiments on freeze drying were done on milk and egg white. Packaged milk from the local market is taken for the experiment. Two sets of experiments were performed. In the first set, three samples of 20 ml milk was used. In the second set, 20 ml sample of egg white was taken. The yolk (the yellow part of an egg) was separated from the egg and the egg white was taken for experiment. Again three samples of egg white were taken for the experiment. Milk and egg white were selected for the experiment because these come under food category, and also they have organic substance and have rich protein.

2.2 Experimental Setup

The experimental setup is a laboratory lyophilizer which consists of a vacuum chamber, in which the pressure is continuously maintained by the help of a vacuum pump. There is a condenser which is used to catch the water vapour and preventing it to enter into the vacuum pump. The block diagram of the experimental setup is shown in Fig. 1. The external and important device which is required is a deep freezer to pre-freeze the sample. The accessories and attachments used for the experiment are conical flasks, rubber tubes, glass connectors and rubber cork. The conical flask acts as a container to place the sample, and when it is attached to the vacuum chamber, it acquires the vacuum pressure. The rubber tubes are used to connect the vacuum chamber with the glass connectors which fit in the cork. The cork makes

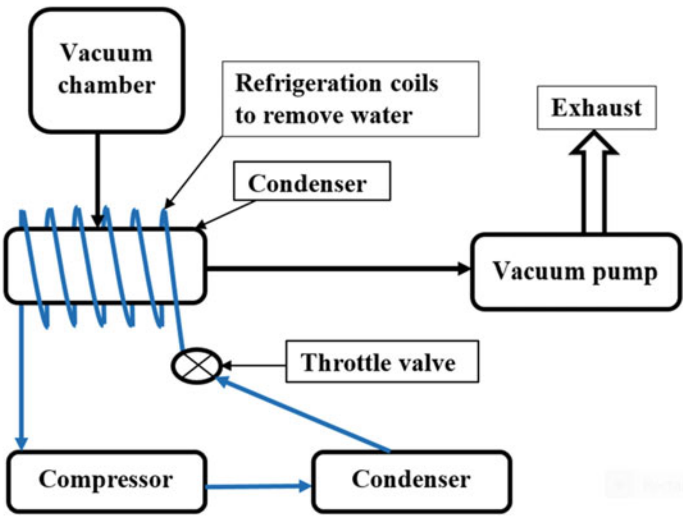

Fig. 1 Block diagram of lyophilizer

the conical flask sealed to the atmosphere and connects to the vacuum chamber. The main features of the lyophilizer are: safety cut-off for the vacuum pump, well arranged ports for placement of flasks, dual stage rotary vane vacuum pump.

2.3 Sample Preparation

Three conical flasks were taken, washed properly and dried. The flasks were fitted with cork and the combined mass of the flask and cork were taken. The combined mass was taken because it is convenient to measure the combined mass during the experiment. Later, for calculation of the mass of the sample, the mass of conical flask and the cork was subtracted from the total mass. For the first experiment, three samples of 20 ml milk were taken, and for the second experiment, three samples of 20 ml egg white were taken in three flasks. The respective corks were tightly put on the flask. The mass of each flask and cork with sample was taken again and noted down. The flasks with the sample were taken to freeze in a deep freezer of a domestic refrigerator. Before putting it inside the deep freezer, the mouth of the flask was sealed tightly so that any loss of moisture can be prevented from the sample. The deep freezer was set to its maximum freezing capacity to freeze it to the lowest possible temperature available with the refrigerator. Once the samples were frozen, they were taken outside, and now, the samples were ready for experiments in the lyophilizer.

2.4 Experiments and Calculations

The lyophilizer was turned ON. The condenser was allowed to reach a stable temperature of −80 °C. The vacuum pump was switched ON and allowed to run the lyophilizer idle for some time till the pressure indicator showed a value of 10 Pa or less. The frozen sample was taken and loaded in the ports available in the vacuum chamber. After waiting for 30 min, the ports were closed, and the sample with the flask and cork was weighed in the weighing balance in least possible time. The samples were again loaded in the lyophilizer. This process was repeated again and again in every 30 min till the reading in the weighing balance shows nearly the same values for last three consecutive readings. The flask and cork masses were subtracted from the raw data to get the actual mass of the sample with time.

The percentage of water loss can be calculated with the tabulated values, and moisture content is calculated by plotting as moisture content versus time.

The moisture content of the sample is calculated by the given simple using the procedures mentioned below.

The mass of sample (m_s) was estimated using,

$$m_s = (m_{sc} + m_c) - (m_{co} + m_c) \tag{1}$$

where, m_{sc} is mass of sample with conical flask, m_c is mass of cork and m_{co} is mass of conical flask.

Total mass of water in the sample (m_T) was estimated using,

$$m_T = m_i - m_d \tag{2}$$

where, m_i is initial mass of sample and m_d is final dried mass of sample.

The mass of water at any given time (m_t) was estimated by subtracting the m_d from mass of sample at a given time.

Moisture content of sample on dry basis (M_{db}) was calculated using,

$$M_{db} = \frac{m_t}{m_d} \tag{3}$$

3 Results and Discussion

The average mass of the sample from three samples was estimated with time in order to reduce any experimental error. The mass loss data, average mass, moisture content on dry basis and total moisture percentage of skimmed milk are calculated and tabulated in Table 1.

The results were plotted and shown in Fig. 2a–c. From Table 2, it can be seen that the moisture decreased with time for 9 h, and after that, there is not much reduction in mass. It shows that the mass reaching its constant value implies that the sample is completely dried. The average mass for the milk with time is plotted in Fig. 2a. The initial mass of the sample (m_i) was 21.3352 g which was reduced to 2.5872 g after 9 h. At the end of 12 h, the complete dried mass (m_d) remained was 2.4625 g. At the end of the drying process, when major part of water content is removed, the process gets slowed because the final water content is adsorbed with the solid matrix. Once the mass was obtained, the moisture content of the sample in terms of dry basis was calculated and shown in Fig. 2b. The initial moisture content in dry basis (db) was 7.6642 kg/kg of db. After 9 h of drying, the moisture content is reduced to 0.66 kg/kg of db. After 10 h of time, the moisture content was almost same, and it is assumed to be dried. The moisture content in terms of total per cent of water content was plotted in Fig. 2c. The moisture content of the milk is reduced to half (50%) in just 2.5 h; it remains 23% after 5 h, 0.66% at 9 h and 0.16% after 10 h of drying time.

Table 2 presents the similar data of egg white, and it consists of the data of three experiments and its average mass. Finally, the moisture content in kg/kg of db and moisture percentage were estimated.

The average mass of the sample, moisture content on dry basis and total moisture percentage are calculated for egg white and tabulated in Table 2 and plotted in Fig. 3a–c. From Table 2, it can be seen that the moisture decreased with time for the first 6 h,

Table 1 Experimental results from three sample of 20 ml milk

Time (h)	Sample-1 (g)	Sample-2 (g)	Sample-3 (g)	Average (g)	kg of water/kg of db	Moisture (%)
0	21.3362	21.3337	21.3357	21.3352	7.6642	100
0.5	18.3519	18.6102	18.613	18.525	6.5229	85.1097
1.0	16.5454	16.5134	16.7606	16.6065	5.7438	74.9442
1.5	14.6539	14.8935	15.1115	14.8863	5.0453	65.8295
2.0	13.1628	13.437	13.6493	13.4164	4.4484	58.0410
2.5	11.4027	11.8318	12.2922	11.8422	3.8091	49.6998
3.0	10.1953	10.5	10.8245	10.5066	3.2667	42.6229
3.5	8.9966	9.5034	9.7165	9.4055	2.8195	36.7886
4.0	7.97	8.4173	8.5975	8.3283	2.3821	31.0809
4.5	7.3686	7.6724	7.8489	7.63	2.0985	27.3808
5.0	6.5538	6.8438	7.0358	6.8111	1.7660	23.0417
5.5	5.7959	6.0338	6.2478	6.0258	1.4471	18.8807
6.0	5.2418	5.447	5.7089	5.4659	1.2197	15.9140
6.5	4.5524	4.7913	4.8947	4.7461	0.9274	12.1000
7.0	3.8849	4.1097	4.3199	4.1048	0.6669	8.7020
7.5	3.4563	3.6385	3.7965	3.6304	0.4743	6.1883
8.0	2.9511	3.1833	3.2842	3.1395	0.2749	3.5872
8.5	2.6414	2.8915	3.001	2.8446	0.1552	2.0246
9.0	2.4353	2.5857	2.7407	2.5872	0.0507	0.6607
9.5	2.434	2.4812	2.6582	2.5245	0.0252	0.3285
10.0	2.433	2.4783	2.5667	2.4927	0.0123	0.1600
10.5	2.4312	2.4761	2.4938	2.467	0.0018	0.0238
11.0	2.4303	2.4753	2.4902	2.4653	0.0012	0.0148
11.5	2.4299	2.474	2.4897	2.4645	0.0008	0.0106
12.0	2.4301	2.473	2.4843	2.4625	0.0000	0.0000

and after that, there is not much reduction in mass. The initial mass (m_i) of 20 ml egg white is estimated as 21.2677 g. As time progresses, the mass reduced due to the removal of water. The mass of the sample becomes 2.7566 g after 6 h of drying. At the end of drying, the final mass of the dried product (m_d) is 2.6127 g. From 6 to 10 h, the curve is flattening which indicates that the product is almost dried after 6 h of drying. The moisture content in dry basis is plotted in Fig. 3b. The initial moisture content is 7.1401 kg of water/kg of db which is reduced to 0.0551 kg of water/kg of db after 6 h of drying. The moisture percentage with time is plotted in Fig. 3c. The moisture content is reduced to 53.6% in the first hour of drying, and it reduced to 23.67% at 2.5 h. After 6 h of drying, it is reduced to 0.77%. The complete drying time to produce solid egg powder is estimated as 10 h.

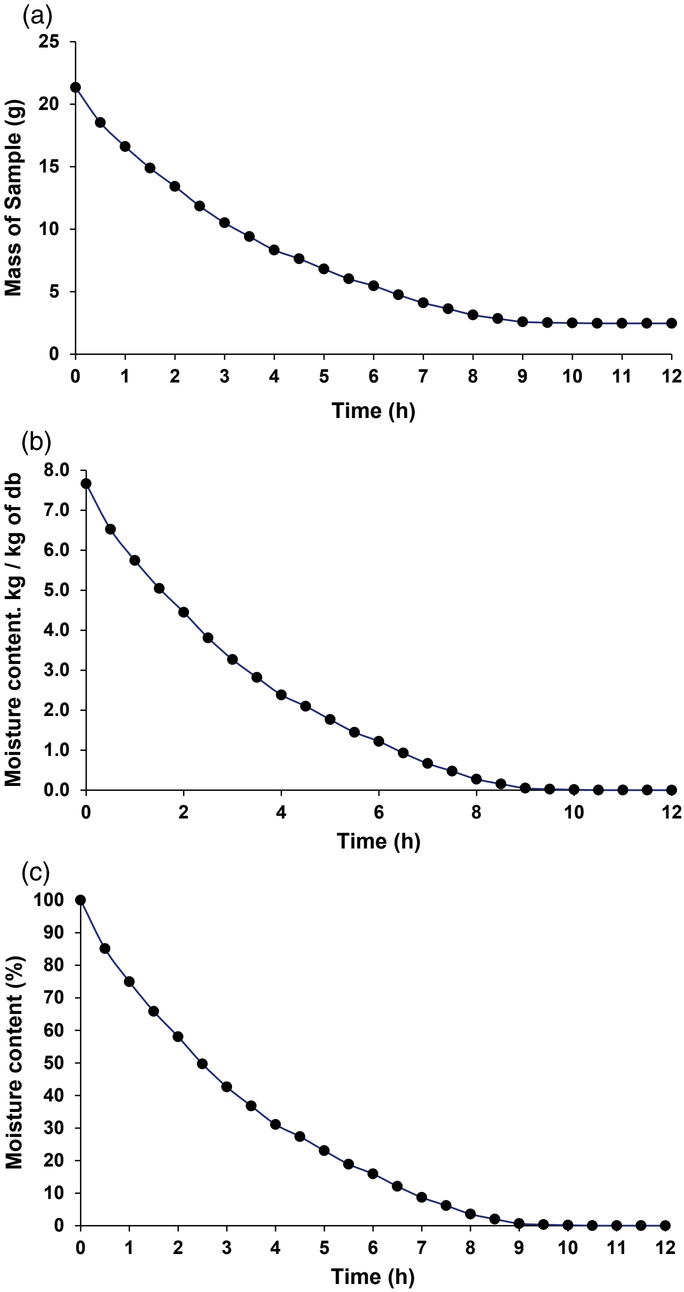

Fig. 2 A **a** Mass of the milk measured during experiment, **b** moisture content of milk in terms of dry basis and **c** moisture content of milk in percentage

Table 2 Experimental results from three samples of 20 ml egg white

Time (h)	Sample-1 (g)	Sample-2 (g)	Sample-3 (g)	Average (g)	kg of water/kg of solid	Moisture (%)
0.0	21.2335	21.4365	21.1332	21.2677	7.1401	100
0.5	16.3785	16.4274	16.5723	16.4594	5.2998	74.2250
1.0	12.5799	12.6272	12.6325	12.6132	3.8276	53.6075
1.5	9.9787	9.7227	9.6336	9.7783	2.7426	38.4113
2.0	8.4093	8.3165	8.4123	8.3794	2.2072	30.9121
2.5	7.0279	6.9373	7.1253	7.0302	1.6908	23.6798
3.0	6.031	5.9792	6.1332	6.0478	1.3148	18.4138
3.5	5.0413	4.9276	5.1375	5.0355	0.9273	12.9872
4.0	4.1764	4.0174	4.3417	4.1785	0.5993	8.3934
4.5	3.7729	3.6725	3.7276	3.7243	0.4255	5.9589
5.0	3.2672	3.2584	3.2731	3.2662	0.2501	3.5033
5.5	2.9696	2.8295	2.9894	2.9295	0.1213	1.6982
6.0	2.7558	2.7521	2.7619	2.7566	0.0551	0.7714
6.5	2.7385	2.7363	2.8384	2.7711	0.0606	0.8489
7.0	2.7094	2.7217	2.7139	2.7150	0.0392	0.5484
7.5	2.6726	2.7032	2.7021	2.6926	0.0306	0.4285
8.0	2.6623	2.6743	2.6927	2.6764	0.0244	0.3416
8.5	2.6598	2.6242	2.6782	2.6541	0.0158	0.2217
9.0	2.6591	2.5929	2.6329	2.6283	0.0060	0.0836
9.5	2.6588	2.5892	2.6272	2.6251	0.0047	0.0663
10.0	2.6587	2.571	2.6084	2.6127	0.0000	0.0000

The experimental results obtained for skimmed milk are compared with the numerical results of Naik et al. [6] and are shown in Fig. 4. It is seen that there is a slight deviation in the moisture content. A maximum deviation of 10% is noticed at $t = 4$ h. The deviation increased and again the deviation decreased toward the end of the process. From the numerical result, it is found that the total drying time at 10 Pa and 313 K (40 °C) was 9.25 h. From the experiment, it is found that the drying time is about 10 h.

There may be various reasons for these deviations. As discussed earlier in literature review, at higher chamber temperature, there is slight distortion in the frozen sample and a small amount of froth is formed. Hence, a change in shape occurred and the numerical results are purely calculated on basis of fixed shape. Therefore, the numerical results could not be able to produce the real values.

.

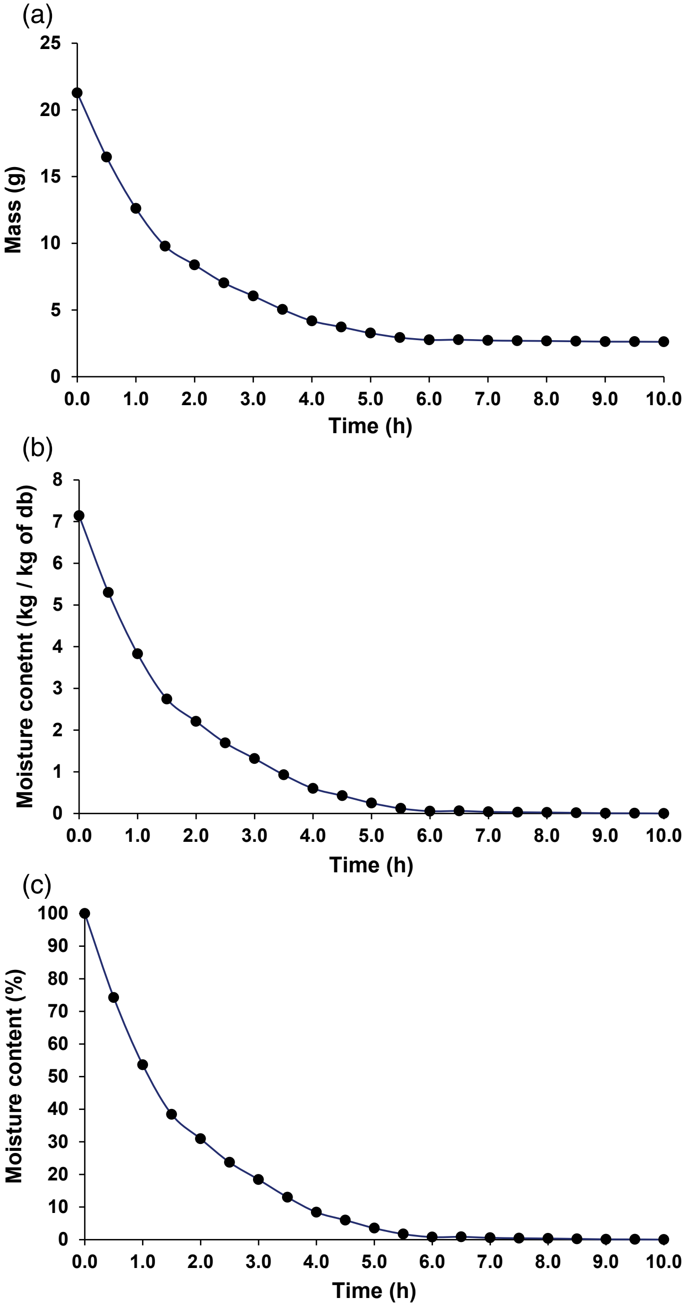

Fig. 3 **a** Mass of the egg white, **b** moisture content of egg white and **c** moisture content in percentage

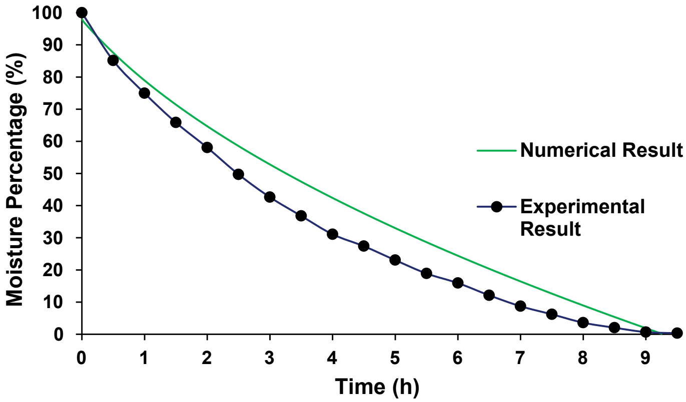

Fig. 4 Numerical results of moisture percentage of skimmed milk [6] compared with present results

4 Conclusion

An experimental analysis of freeze drying was made in this analysis. Milk and egg white were used as sample objects. A table top lyophilizer was used for freeze-drying experiments. A domestic deep freezer was used to freeze the food materials. The following important conclusions were obtained.

The average initial mass of milk was 21.3352 g, and the same of egg white was 21.2677 g. The mass of the samples was reduced when the drying time was increased for both experiments with milk and egg white. The moisture content was reduced to 50% during the first 2.5 h drying time. It reached to 25% approximately at 4.75 h. At 9 h, the change of mass was almost vanished, but the moisture percentage of 0% was obtained at 12 h. Therefore, it is concluded that at 12 h, the milk reached its solid powdered state.

The moisture percentage of egg white was reduced to 74% within 0.5 h. It reached to 53% at 1 h, 31% at 2 h and 3.5% at 6 h. A constant drying rate was noticed from 6 to 10 h of drying time. The moisture percentage reached to 0% at 10 h, and therefore, it is concluded that the egg white reached its solid powdered state at 10 h. The results were compared with existing numerical case and found a good agreement.

References

1. I. Liapis, R. Bruttini (2006) Freeze drying in handbook of industrial drying. In: Mujumdar AS (ed) CRC Press, Taylor and Francis group, 257–281
2. Thijssen HAC (1971) Flavour retention in drying preconcentrated food liquids. J Appl Chem Biotech 21:372–377
3. Toei R, Okazaki M, Asaeda M (1975) The stability of plane sublimation and a model of zone sublimation in freeze-drying of porous bodies. J Chem Eng Jpn 8:282–288

4. Millman MJ, Liapis AI, Marchello JM (1985) An analysis of the lyophilization process using a sorption-sublimation model and various operational policies. AIChE J 31:1594–1604
5. Pikal MJ, Shah S (1990) The collapse temperature in freeze–drying: dependence on measurement methodology and rate of water removal from the glassy state. Int J Pharm 62:165–186
6. Naik R, Arun SG, Chandramohan VP (2017) Numerical simulation for freeze drying of skimmed milk with moving sublimation front using tri diagonal matrix algorithm. J Appl Fluid Mech 10(3):813–818. https://doi.org/10.18869/acadpub.jafm.73.240.27054
7. Roos YH (1992) Phase transitions and transformations in food systems, in handbook of food engineering. In: Heldman DR, Lund DB Marcel Dekker, New York, 145–197
8. Genin N, Rene F (1995) Analyse du Role de la transition vitreuse dans les procedes de conservation agroalimentaires. J Food Eng 26:391–408
9. Quiroga EL, Antelo LT, Alonso AA (2012) Time-scale modeling and optimal control of freeze–drying. J Food Eng 111:655–666
10. Sadikoglu H, Liapis AI (1997) Mathematical modelling of the primary and secondary drying stages of bulk solution freeze-drying in trays: parameter estimation and model discrimination by comparison of theoretical results with experimental data. Drying Technol 15:791–810
11. Mascarenhas WJ, Akay HU, Pikal MJ (1997) A computational model for finite element analysis of the freeze–drying process. Comput Methods Appl Mech Eng 148:105–124
12. Trelea C, Passot S, Fonseca F, Michele M (2007) An interactive tool for the optimization of freeze–drying cycles based on quality criteria. Drying Technol 25:741–751
13. Hammami, Rene F (1997) Determination of freeze-drying process variables for strawberries. J Food Eng 32:133–154
14. Nakagawa K, Ochiai T (2015) A mathematical model of multi-dimensional freeze-drying for food products. J Food Eng 161:55–67
15. Duan X, Zhang M, Mujumdar AS, Wang S (2010) Microwave freeze drying of sea cucumber (Stichopus japonicus). J Food Eng 96:491–497
16. Nastaj JF, Witkiewicz K (2009) Mathematical modeling of the primary and secondary vacuum freeze drying of random solids at microwave heating. Int J Heat Mass Transf 52:4796–4806
17. Crank J (1984) Free and moving boundary problems. Clarendon Press, Oxford, UK
18. Liapis R, Bruttini A (1994) Theory for the primary and secondary drying stages of the freeze-drying of pharmaceutical crystalline and amorphous solutes: comparison between experimental data and theory. Sep Technol 4:144–155
19. Pikal MJ, Roy ML, Shah S (1984) Mass and heat transfer in vial freeze-drying of pharmaceuticals: role of the vial. J Pharm Sci 73:1224–1237