Chapter 6

Moisture sorption isotherm (MSI) and antioxidant stability of optimized product during storage

6.1 Introduction

Extrusion cooking also known as high-temperature short time (HTST) processing technique, is gaining attention for novel food product development due to low-cost and high efficiency continuous cooking process.[28,3,12] In extruded foods base material used are cereals, starches, pulses and vegetable proteins mainly. Since these ingredients help to obtain structure, texture, bulk, mouth feel and various other characteristics desired for the final products.[20]

Moisture content in the food products can be used as the critical data which can evaluate the quality of products during food preservation. The quality of product totally depends upon the moisture content, moisture migration, or moisture uptake. Sorption or desorption state depends on vapor pressure of water present in the sample and surroundings. Equilibrium moisture content (EMC) increases with relative humidity (RH %) but decreases with increase in temperature in a particular food products. The phenomenon wherein the EMC during the adsorption and during the desorption process is different is termed as ‘‘hysterisis.’’.[22]

Water adsorption by any food products is a process where water molecules progressively and reversibly combine with the solids via chemisorption, physical adsorption, and multilayer condensation.[35] There are three region in an isotherm namely region A, B and C. In region A, water represents strongly bound water with enthalpy of vaporization considerably > pure water. The bound water (unfreezable) includes structural water (H-bonded water) and monolayer water.[17] In region B, water molecules bind less firmly. Also vaporization enthalpy is found to be slightly > pure water. Water in region C is loosely bound with the food materials.[22,23]

The moisture sorption isotherm (MSI) study is an important tool which can be used to predict the product stability, improve storing method and selection of packaging material.[4] It is also used to optimize or maximize the retention of color, flavor, texture, nutrients and biological stability.[29] Sorption isotherms of MSI information can be used to design, modelling and optimization of different processes like aeration, drying and storage respectively.[5,16] Silva et al.[30] stated that biomaterials behave as hygroscopic showed problem with moisture content and humidity and change its moisture content according to the humidity and temperature of surroundings.

6.2 Materials and methods

6.2.1 Raw materials

Optimized extruded sample was prepared by using twin extruder. Antioxidant stability during storage and MSI studies were carried in optimized sample.

6.2.2 Antioxidant stability during storage

Total phenolic content (TPC) of extruded product was evaluated during storage by using method described by Slinkard and Singleton.[34] The pre-weighed petri dishes with samples (2g) were placed in hermetically sealed glass desiccators using Na Cl (75% RH) and stored at 25˚C. The analyses of TPC was done at every 15 days interval for 120 days.[32]

6.2.3 Moisture sorption isotherm (MSI) studies

Moisture sorption isotherm (MSI) for red rice incorporated with passion fruit powder (O) extruded product was determined by Smith [32] method and later described by Plahar and Leung.[25] Products were dried at 70˚C for 24 h prior to equilibrating them. Three (25˚C,35˚C and 45˚C) different temperatures, eight saturated electrolytes solution *viz.*, lithium chloride (LiCl), magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), magnesium nitrate ($Mg(NO_3)_2$), potassium iodide (KI), sodium chloride (Na Cl), potassium chloride (KCl) and potassium sulfate K_2SO_4), relative humidity (RH %) range from 11 to 97 % were used during MSI studies. Samples (2 g) were placed into a sterilized pre-weighed petri plates dishes in separate desiccators.[7] Equilibrium data was obtained after attaining three successive weight measurements which did not differ more than 0.001 g. Inside the each desiccator, 10 mL of beaker containing toluene was placed in order to prevent microbial spoilage.[8] The weight of each Petri dish containing samples was measured in 4 days interval. A graph was plotted following equilibrium moisture contents (EMC) *vs* water activity. Table 6.1 illustrated the list of salts solution with respective RH (%). The final equilibrium moisture content (EMC) was calculated by method described by Sant'Anna et al.[33] measuring the difference in the weight loss before and after drying the weight of sample at 105˚C for 3 h in a laboratory oven (Boi-Technics India). The relationship between equilibrium relative humidity (ERH) and water activity (a_w) is shown below.[31]

$$a_w = \frac{ERH}{100}$$

6.2.4. Mathematical model fitting and data analysis

Existing mathematical models were reviewed and used to predict the adsorption monolayer moisture content at different temperatures. The experimental values of EMC and ERH were obtained from experiment. Six mathematical models (Table 6.1) were fitted to experimental data (EMC versus a_w) and the constants. The models were calculated by nonlinear regression using MATLAB (Math Works, Inc., R2008a).Various researchers have been extensively using these isotherm models in food products.[9, 26] The goodness of fit and precision of selected models were on the basis of high coefficient of determination (R^2) and low root mean square error (RMSE).

Table 6.1 Equilibrium relative humidity of selected salt solution at various temperature levels[13]

RH (%) at temperature			
Saturated salt solution used	25 ˚C	35˚C	45˚C
Lithium chloride (LiCl)	11.30	11.25	11.16
Magnesium chloride ($MgCl_2$)	32.78	32.05	31.10
Potassium carbonate (K_2CO_3)	43.16	43.17	43.17
Magnesium nitrate ($Mg(NO_3)_2$)	52.89	49.91	46.93
Potassium iodide (KI)	68.86	66.96	65.26
Sodium chloride (NaCl)	75.29	74.87	74.52
Potassium chloride (KCl)	84.34	82.95	81.74
Potassium sulfate (K_2SO_4)	97.30	96.71	96.12

Table 6.2 Mathematical models used to fit the equilibrium moisture sorption isotherm of optimized product

Sl.no.	Model	Mathematical equation	Reference
1	Oswin	$M_W = A(\frac{a_w}{1-a_w})^B$	Andrade et al.[1]
2	Smith	$M_W = A + B\ln(-a_w)$	Andrade et al.[1]
3	Curie	$M_W = \exp(A + Ka_w)$	Curie [10]
4	Peleg	$M_W = Aa^c{}_w + Ba^k{}_w$	Basu et al.[4]
5	Langmuir	$\frac{1}{CM_o} = a_w(\frac{1}{M_w} - \frac{1}{M_O})$	Langmuir [18]
6	Brunauer-Emmett-Teller (BET)	$\frac{M}{M_0} = \frac{Ca_w}{(1-aw)[1+(C-1)a_w]}$	Brunauer et al.[6]

Note: $M_{w:}$ equilibrium moisture content (g water/100 g dry matter) and M_o : monolayer sorbet constant and a_w represent the water activity (decimal). A, B, K and C are respective model constants.

6.3 Results and discussion

6.3.1 Antioxidant stability during storage

The product was extruded from combination of pigmented rice and exotic fruit (passion fruit foam mat dried powder). Antioxidant stability (TPC) during storage of optimized product are presented in Fig.6.1 and values are stated in Table 6.3. From the Fig.6.1, it can be concluded that TPC (mg GAE/100 g of dry solid) showed amount of total phenolic acid changes was very less with respect to storage duration (120 days). Antioxidant and phenolic compounds degradation are affected by various parameters *viz.*, light, temperature, air oxidation phenomenons, etc. [36]

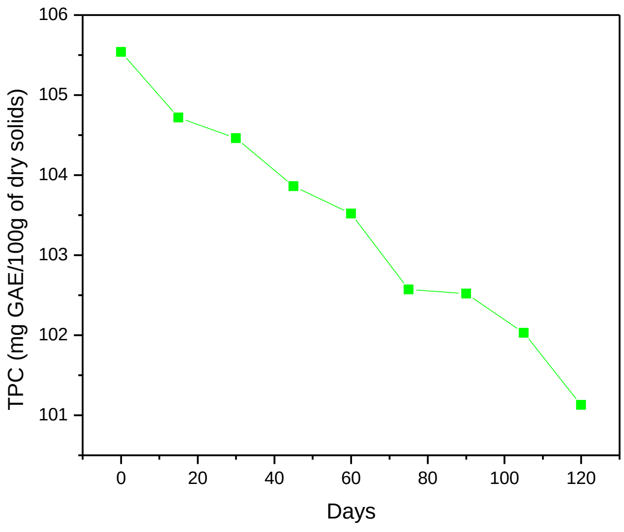

Fig. 6.1 Antioxidant stability during storage of sample

Table 6.3 Storage study of antioxidant stability of TPC

Total Days	Total phenolic content (mg GAE/100 g dry matter)
0	105.54±0.40
15	104.72±0.45
30	104.46±0.23
45	103.86±0.18
60	103.52±0.47
75	102.57±0.32
90	102.52±0.31
105	102.03±0.02
120	101.13±0.08

Note: values were calculated in triplicates (n=3) as mean ± SD

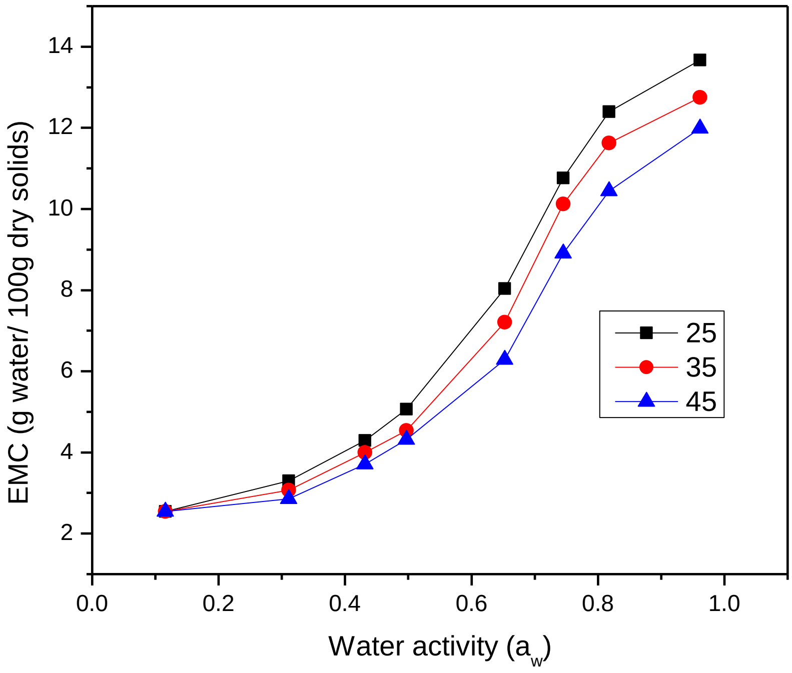

Fig 6.2 Moisture sorption isotherm (MSI) of optimized sample at three different temperatures

MSI of optimized sample at different temperatures (25C˚, 35˚C and 45˚C) are presented in Fig 6.2. The shape of the graph resembles more of Sigmoid S-shaped curves of type II types at given temperatures between water activity and EMC (dry basis) data. Many researchers have also concluded similar finding extruded products.[19, 24] Initially, slow increase in EMC was observed until 0.6 a_w and after that abrupt increase in graph was observed. Initial slow increase might be attributed to the hydrophilic nature of carbohydrates and protein in extrudate. At higher temperature, the possibilities of reduction in active sites for water binding may occur which leads to decrease EMC. Also, water molecules in the extrudates attain higher energy levels and smash away from the water binding sites, eventually led to lower EMC.[27] Demertzis et al.[11] also stated that above mentioned situation make the food material less hygroscopic at higher temperatures. In starchy food products, crystalline regions of starch (amylopectin) are reported to be unaffected to moisture diffusion process and therefore, increase in EMC may act as a plasticizers for amylose region (amorphous).[2]

6.3.2 Mathematical modeling and fitting of moisture sorption data

The sorption isotherm models, their respective constants and statistical parameters are presented in Table 6.4. The EMC values were obtained from experimental data of control and optimized extruded products at three different temperatures (25-45˚C) and water activity (a_w) ranged 0.11 to 0.97 were fitted to six MSI models. Mathematical models used were Oswin, Smith, Curie, Peleg, Langmuir and Brunauer-Emmett-Teller (BET). The model constants and statistical parameters were showed in Table 6.4 (R^2, Adj.R^2, RSME and SSE) and from the value best fit was predicted. In the optimized extruded sample, at 25˚C Langmuir model showed R^2 0.98, adj. R^2 0.97, RSME 0.62 and SSE 2.35, at 35 ˚C Peleg model showed R^2 0.99, Adj. R^2 0.99, RSME 0.33 and SSE 0.44 and finally at 45 ˚C, it was recorded that R^2 0.99, adj. R^2 0.98, RSME 0.45 and SSE 0.83. Therefore, from the data, it can be determined that at 25 ˚C, Langmuir model and at 35 and 45 ˚C, Peleg model showed better fitting during the prediction of EMC of extrudate. Various researcher reported that Peleg model showed better suitable model during the prediction of EMC of starchy powders e.g. yam, [21] potato [15] and pistachio nut [14] at different storage temperatures.

Table 6.4 Sorption isotherm models and their respective constants and statistical parameters

Storage temperature 25˚C									
Model	**Model coefficients/constants**					**Goodness of fit parameters**			
	A	**B**	**K**	**C**	**M_o**	**R2**	**Adj. R^2**	**RSME**	**SSE**
Oswin	6.43	0.24				0.8	0.77	2.04	25.19
Smith	6.36	0.23	-	-	-	0.43	0.34	3.46	72.14
Curie	1.89	0.02	-	-	-	0.39	0.29	3.59	77.32
Peleg	-109.5	123.8	1.16	1.15	-	0.98	0.96	0.79	2.5
Langmuir	-	-	-	0.73	3.01	0.98	0.97	0.62	2.35
Brunauer-Emmett-Teller (BET)	-	-	-	0.001	3.11	0.96	0.96	0.83	4.16
Storage temperature 35˚C									
Oswin	5.85	0.25	-	-	-	0.87	0.85	1.37	11.39
Smith	6.03	2.18	-	-	-	0.95	0.95	0.8	3.85
Curie	0.76	-	1.88	-	-	0.98	0.98	0.5	1.53
Peleg	0.66	12.64	1.39	-0.35	-	0.99	0.99	0.33	0.44
Langmuir	-	-	-	0.002	3.22	0.97	0.97	0.62	2.34
Brunauer-Emmett-Teller (BET)				0.003	3.19	0.98	0.98	0.47	1.34
Storage temperature 45˚C									
Oswin	5.8	0.26	-	-	-	0.91	0.9	1.08	7.07
Smith	5.51	0.33	-	-	-	0.61	0.55	2.36	33.6
Curie	0.78	-	1.86	-	-	0.39	0.29	3.59	77.32
Peleg	8.33	5.71	3.72	0.64	-	0.99	0.98	0.45	0.83
Langmuir	-	-	-	0.002	3.18	0.96	0.95	511	3.38
Brunauer-Emmett-Teller (BET)	-	-	-	0.005	3.15	0.98	0.97	0.54	1.76

Note: M_w : monolayer moisture content (g water/100 g dry matter) and M_o : monolayer sorbet constant and a_w represent the water activity (decimal). A, B, K and C are respective model constants.

6.4 Conclusion

Total polyphenols content (TPC) of extrudate showed slow degradation of antioxidant content. The sorption isotherm study of extrudate at three different temperatures (25-45˚C) and a_w level (ranged from 0.11-0.97) were carried out by standard static-gravimetric method using various salt solutions revealed Sigmoid shape resembling type II isotherm was observed which is very typical of food material. Six model fitting concluded that at 25 ˚C Langmuir model showed the best fit. And at 35 ˚C and 45 ˚C Peleg model predicted as most suitable model to practice MSI study of optimized extrudate.

Reference

[1] Andrade, P, R, D., Lemus, M,R. and Perez, C,C,E. Models of sorption isotherms for food: uses and limitations. *Vitae, Revista De La Facultad De Quimica Farmaceutica*, 18(3):325-334, 2011.

[2] Al-Muhtaseb, A,H., McMinn, W,A,M. and Magee, T,R,A. Moisture sorption isotherm characteristics of food products: a review. *Food Bio production Processing*, 80(2):118-128, 2002.

[3] Abd el-hady, E,A., Mostafa, G,A., El-samahy, S,K. and El-saies, I,A. Production of high fiber corn extrudates. *Journal of Agricultural Science, Mansoura University*, 23:1231-1245,1998.

[4] Basu, S., Shivhare, U, S. and Mujumdar, A, S. Model for sorption isotherm for food: A review. *Drying Technology*, 24(8):917-930, 2006.

[5] Bala, B, K. Physical and thermal properties of malt. *Drying Technology*, 9(4):1091-1104,1991.

[6] Brunauer, S., Emmet, P,H. and Teller, E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60:309-319, 1938.

[7] Bisharat, G,I., Eleni, P, N., Panagiotou, N, M., Krokida, M, K. and Maroulis, Z, B. Thermal, textural, and physicochemical analysis of corn extrudates enriched with broccoli or olive paste. *International Journal of Food Properties*, 17(9):2100-2116,2014.

[8] Cassini, A, S., Marczak, L, D, F. and Norena, C,P, Z. Water adsorption isotherms of texturized soy protein. *Journal of Food Engineering*, 77:194-199,2006.

[9] Cardoso, J, M. and de Silva P, R. Hygroscopic behavior of banana (*Musa ssp*. AAA) flour in different ripening stages. *Food Bio production and Processing*, 92(1):73-79, 2014.

[10] Caurie, M. Derivation of full range moisture isotherms. In Water Activity: Influences on Food Quality (L.B. Rockland and G.F. Stewart, eds.) pp. 63-87, Academic Press, New York,1981.

[11] Demertzis, P, G., Riganakos, K, A. and Kontaminas, M, G. Water sorption isothermsfor crystalline raffinose by inverse gas chromatography. *International Journal of Food Science and Technology*, 24:629-636, 1989.

[12] Ding, Q., Ainsworth, P., Tucker, G. and Marson, H. The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-based expanded snacks. *Journal of Food Engineering*, 66:283-289, 2005.

[13] Greenspan, L. Humidity fixed points of binary saturated aqueous solutions. Journal of Research, National Bureau of Standards (US), Series A, Physics and Chemistry, 81:89-96,1977.

[14] Hayoglu, I. and Faruk, O, G. Water sorption isotherms of pistachio nut paste. *International Journal of Food Science*, 42:224-227, 2007.

[15] Iguedjtal, T., Louka, N. and Allaf, K. Sorption isotherms of potato slices dried and texturized by controlled sudden decompression. *Journal of Food Engineering*, 85:180-190,2008.

[16] Kumar, P. and Mishra, H, N. Moisture sorption characteristics of mango-soy fortified yogurt powder. *International Journal of Dairy Technology*, 59:22-28,2006.

[17] Kinsella, J, E. and Fox, P,X. Water sorption by proteins: milk and whey proteins. CRC, *Critical Reviews in Food Science and Nutrition*, 24:91-139,1986.

[18] Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40:1361-1402, 1918.

[19] Lazou, A. and Krokida, M. Thermal characterization of corn-lentil extruded snacks. *Food Chemistry*,127: 1625-1633,2011.

[20] Launay, B. and Lisch, J, M. Twin-screw extrusion cooking of starches: Flow behavior of starch pastes, expansion and mechanical properties of extrudates. *Journal of Food Engineering*, 2: 259-80, 1983.

[21] Montes, E., Torres, R., Andrade, R., Perez, O., Marimon, J. and Meza, I. Models of desorption isotherms of yam (*Dioscorea rotundata*). *Dyna*, 72:145-152,2009.

[22] Mujumdar, A, S. and Devahastin, S. Fundamental principles of drying. In Mujumdar's Practical Guide to Industrial Drying; Devahastin, S., Ed.;Exergex Corp: Montreal,1-22,2000.

[23] Mujumdar, A,S. Ed. Handbook of Industrial Drying, 3rd Enhanced Ed; CRC Press: Boca Raton, FL, 2006.

[24] Norajit, k., Gu, B. and Ryu, G. Effects of the addition of hemp powder on the physicochemical properties and energy bar qualities of extruded rice. *Food Chemistry*, 129:1919-1925, 2011.

[25] Plahar, W, A. and Leung, H, K. Storage stability of dehydrated and Soy-fortified fermented maize meal. *Journal of Food Science*, 50:182-187,1985.

[26] Peng, G., Chen, X, Wu. and Jiang, X. Modeling of water sorption isotherm for corn starch. *Journal Food Engineering*, 80(2):562-567, 2007.

[27] Palipane, K, B. and Driscoll, R,H. Moisture sorption characteristics of in shell macadamia nuts. *Journal of Food Engineering*, 18:63-76, 1992.

[28] Ryu, G, H., Neumann, P, E. and Walker, C,E. Effects of some baking ingredients on physical and structural properties of wheat flour extrudates. *Cereal Chemistry*, 70:291-297,1993.

[29] Rizvi, S, S, H. Thermodynamic properties of foods in dehydration. In M, A, Rao, and S, S.,H. Rizvi (Eds.), Engineering properties of foods (pp. 223-309). New York: Marcel Dekker,1995.

[30] Silva, C, de L, O,C., Faria, L, J,G, de. and Costa, C, M, L. Comportamento higrosc opico de partes aereas de pimenta-de-macaco (*Piper aduncum* L.). *Revista Brasileira de Engenharia Agrícola e Ambiental*, 19(4):376-381,2015.

[31] Sahin, S. and Sumnu, S,G. Water activity and sorption properties of foods. In Physical Properties of Foods, S. Sahin and S.G. Sumnu, eds. pp. 193-226, Springer Science1Business Media, New York, 2006.

[32] Smith, P. The determination of equilibrium relative humidity or water activity in foods. A literature review, BFMIRA, Leatherhead, 29p,(Scientific and Technical Surveys,70),1971.

[33] Sant'anna, V., Englert, A, H., Correa, A,P,F., Brandelli, A., marczak, L,D,F. and Tessaro, I,C. Grape marc powder: Physicochemical and microbiological stability during storage and moisture sorption isotherm. *Food Bioprocess and Technology*, 7:2500-2506, 2014.

[34] Slinkard, K. and Singleton,V, L. Total phenol analysis: Automation and comparison with manual methods. *American Journal of Enology and Viticulture*, 28:49-55, 1977.

[35] Van den B, C. and Bruin, S. Water activity and its estimation in food systems: Theoretical aspects. In Water Activity: Influences on Food Quality; Rockland, L.B., Stewart, G.F., Eds.; Academic Press: NewYork, 1-61,1981.

[36] Yousif, A., Durance,T,A., Scaman, C,H. and Girard, B. Headspace volatiles and physical characteristics of vacuum microwave, air, and freeze-dried oregano (*Lippiaber landieri Schauer*). *Journal of Food Science*, 65(6):926-930, 2000.