CHEMICAL ENGINEERING TRANSACTIONS

VOL. 55, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Tichun Wang, Hongyang Zhang, Lei Tian

ISBN 978-88-95608-46-4; **ISSN** 2283-9216

DOI: 10.3303/CET1655041

Experimental Study of Freeze-thaw Cycles Placement in Heat Pump Drying of Tilapia Fillets

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Freeze-thaw placement in the drying process can reduce the average drying temperature of the sample. In order to speed up the drying process and maintain a good drying quality of dry tilapia fillets which were achieved in the condition of freeze-thaw cycles placement in a heat pump drying process, a series of drying tests were studied by using the drying time points as the variables in drying process. Freeze-thaw parameters of 4-7 (twice placement) drying time point were optimized by $L9(3^4)$ orthogonal experiment at 7^{th} hours of drying. The results showed when freeze-thaw were placed into the process of heat pump drying process which could improve the quality of dried tilapia fillets effectively. The best quality indicators under optimal condition were as follows: The value of Ca^{2+}-ATPase activity, rehydration rate, whiteness and hardness was 2.75 μmol Pi/mg prot/h, 34.32 %, 38.87 and 10.0 N, respectively. The comprehensive score of optimizing process was 99.27. which has been improved 17% compared to the control sample. This result can provide a new low temperature drying technology and a reference for similar aquatic products.

1. Introduction

Heat pump drying is a good method which can provide low-temperature in the aquatic products dehydration process (Li et al, 2016; Roselli et al., 2016; Cucumo et al., 2016), in addition to freeze-dried (Dordoni et al, 2015). However, in the process of drying, with the surface of water vaporization and dry layer expanding to the food inside, drying surface gradually shrinks which lead to a more compacted organizational structure. Coupled with the increased bound water proportion substantially and grown outward diffusion of water vapor resistance, the removal of internal moisture is becoming difficult (Geert, 2015). Continuous liquid film layer becomes pieces of discontinuous wet area. The mass transfer coefficient of the surface, evaporation and drying rate decrease. At the same time, the samples also show deterioration of partial hard and drying quality. The elevated drying temperature accelerates the drying process, but it will decrease the quality of color, hardness, taste, etc. Changing the drying conditions is a common way to maintain a product quality (Santacatalina et al, 2016). Freeze-thaw, as a pretreatment way, has been gotten a certain application in the dried fruits and vegetables processes (Zielinska et al, 2015). In addition, freezing and thawing involve multiple freeze-thaw cycles, people have focused on the studies of freeze-thaw cycles negative impact on the quality of frozen food (Javid et al, 2014). Freeze-thaw cycles effect research on the gel structure and performance showed that freeze-thaw can effectively improve the gel properties. In the puffing sweet potato products, with the increase of freeze-thaw placement times, the porous condition is easily to be formed, and the structure is loosened. Whether freeze-thaw process is applied to drying processing of meat food, is also rarely reported.
From the previous studies, It can be concluded that freeze-thaw pretreatment accelerates the drying rate effectively and the properties of samples had been improved under appropriate freeze-thaw condition of pretreatment (Li et al., 2014). In order to further obtain the combined effects of freeze-thaw process into heat pump drying, this study adopted the method of freeze-thaw cycles placed under the tilapia fillets heat pump drying process. By monitoring and measuring the quality of dried products under the drying process, the properties of dried tilapia fillets are explored.

Please cite this article as: Li M., Guan Z.Q., Xie D.J., 2016, Experimental study of freeze-thaw cycles placement in heat pump drying of tilapia fillets, Chemical Engineering Transactions, 55, 241-246 DOI:10.3303/CET1655041

2. Material and methods

2.1 Main materials and reagents

Materials: fresh tilapia, purchased from Zhanjiang Gongnong market, weighing about 0.75kg/bar, Fish fillet specifications: 100 mm×50 mm×5 mm.

Reagents: Adenosinetriphosphatase assay kits and Coomassie brilliant blue G250 protein fast stain kits from Nanjing Jiancheng Bioengineering Institute.

2.2 Main instruments and equipment

Self-built heat pump drying device:3P power, temperature -20-80°C, humidity 20%-80%; HHS-type electric heated water bath, Shanghai Industrial Corporation Limited, China. Boxun medical equipment factory; DZF-6050 vacuum oven, Shanghai Jing Hong Laboratory Instrument Corporation Limited. China; BD-730LT-86L-I ultra-low temperature freezer, Qingdao Haier Group, China; FYL-YS-50L incubator, Beijing Fuyi Electric Corporation Limited.. China; T-18 homogenizer, Germany IKA group; GL-10LMD refrigerated centrifuge, Hunan Xingke Scientific Instrument Corporation Limited., China; Sigma 1-14 high-speed desktop centrifuge, Germany Sigmal Company, Germany; UV-8000 UV-visible spectrophotometer, Shanghai Yuanxi Analysis Instrument Corporation Limited.. China; CR-10 handheld colorimeter, Japan Konica Minolta Holdings, Inc. Japan; TMS-PRO texture analyzer, U.S.FTC Company, America; AY120 analytical balance, Shimadzu Corporation, Japan.

2.3 Methods

Single-factor Test of Placement Points and Times

Optimal pretreatment condition of freezing and thawing has been obtained from preliminary experiments. These pretreatment condition is freezing temperature -32°C, melting temperature 20°C, freezing time 1.0 h, thawing time 1.5h respectively, as pretreatment conditions on the same specifications of fresh tilapia fillets and freeze-thaw placement at different period of time under the heat pump drying process. Considering the entire range of drying period of time, placement points are set at 1st, 4th, 7th hours. Drying is to be ended when dry basis moisture content reaches 0.30 ± 0.02g/g, then the quality of dried products is measured. The time of freeze-thaw process is excluded from the whole drying period. The experimental design showed in table 1.

Table 1: The list of the placement points and times for freeze- thawing process

The number of implantation	Test number	Insertion points (drying time points)		
		1 h	4 h	7 h
	1	✓		
1	4		✓	
	7			✓
	1-4	✓	✓	
2	1-7	✓		✓
	4-7		✓	✓
3	1-4-7	✓	✓	✓

Note**:** ✓Indicates that freeze-thaw process is placed into this point.

Orthogonal Optimization of Placement Points for Freeze-thaw Process

Based on single-factor test results, orthogonal experiment was placed at 7^{th} hours to determine the best freeze-thaw process under the condition of each point. Table 3 shows the results of the orthogonal experiment.

Indicators and Evaluation Methods

The methods of rehydration rate, activity of Ca^{2+}-ATPase, whiteness, hardness were agreed with that of literature (Li et al, 2014).

Determination of drying rate curves: The drying rate represents the average changes of dry basis moisture content in per unit time. In order to reflect the rate of drying, the drying rate curves were plotted. The average drying rate was calculated by the formula as follows:

$$v = (w_2 - w_1)/(t_2 - t_1) \quad (1)$$

Where, v is the rate of drying; w_1, w_2, respectively, represent the moisture content on a dry basis (g/g) in t_1 and t_2; t_1, t_2 are the drying time (h).

Comprehensive scoring methods: For rehydration rate, activity of Ca^{2+}-ATPase and whiteness, the greater these values, the better quality of dried products. The hardness of rehydrated fillets was greater than that of fresh (7.4 ± 0.55 N). Generally, it's better for dried products after rehydration was close to that of fresh. So the

smaller of hardness, the better quality is. Out of 100 points in total, the scores of rehydration rate and activity of Ca^{2+}-ATPase both set at a = 30 points, whiteness and hardness at a = 20 points.
For rehydration rate, activity of Ca^{2+}-ATPase and whiteness indexes, was calculated as follows:

$$Y_i = a \cdot \frac{W_i}{W_0} \tag{2}$$

For hardness, being calculated as follows:

$$Y_i = a \cdot \frac{W_0}{W_i} \tag{3}$$

Where, Y_i refers the weighted score for the index; a refers weighting of scores for the indicators; W_0 represents the optimum value in this set of experiments; W_i stands for the actual measured value for each test index.

Statistical Analysis

All the tests were conducted in triplicate and data were sorted. Standard deviation was also calculated. Analysis of variance was used to evaluate significant differences (P <0.05) between the means for each sample.

3. Results and discussion

3.1 Effect of freeze-thaw placement points and times on the drying time and drying rate

Optimum freeze-thaw conditions was obtained in the pretreatment as the values of all freeze-thaw process, without freeze-thaw placement treatment as control group, placement points and times as the variables, all analysis were conducted in triplicate. Figure 1 shows effect of freeze-thaw placement points and times on the drying time and drying rate.

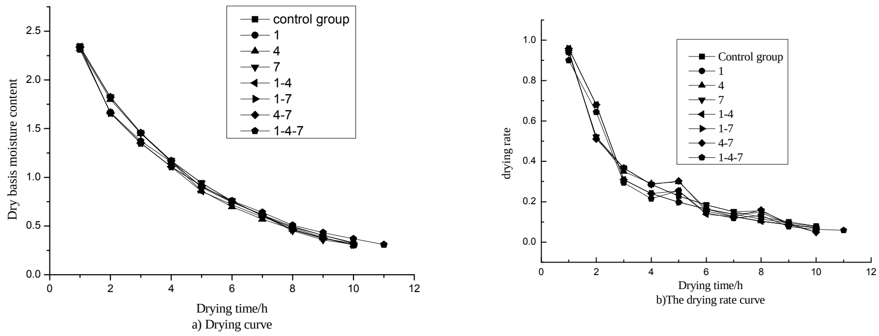

Figure1: The curves of tilapia fillets heat pump drying rate under different placement points and times for freeze-thawing process

It can be seen from Figure 1a, the effect of freeze-thaw placement points and times on the drying time was limited. After placing three times, the time for tilapia drying to the same moisture content increased 1 h alternatively. From Figure 1b, Curves of the drying rate decreased with time. The temperature conditions of the control group could provide better protection to the mass transfer in a certain time when freeze-thaw cycles were placed into the drying. While excessive freeze-thaw placement caused the average temperature of the entire drying process lower than other experimental groups. From figure 1b could also see that drying rate was rebounded in a short period of time after freeze-thaw placement. It perhaps freezing process caused the adsorbed water and bound water which are difficult to remove in the drying process to release. After thawing treatment, these parts of water were separated from the food tissue more easily. The closer placement point in the last drying time, the smaller the recovery magnitude of the drying rate. Because of the highwater content in the early period of drying, water permeation rate was greater than the rate of moisture migration caused by simple drying. In addition, bound water released into freedom water after freeze treatment (Rodiño-Arguello et al., 2015; Wu et al, 2016). Therefore, drying process after freeze-thawing process would be a large number of moisture removal. The proportion of bound water increased sharply and the overall moisture content rate was significantly lower than the before at the last time of drying. On the other hand, the free water content inside and outside of the cells reduced, production of ice crystals decreased, the moisture permeation rate caused by freeze was close to the moisture migration rate caused by simple drying. Additionally, drying late, the advantage of freeze had disappeared, Fish fillets shrinkage caused organization form dense, pore was not smooth with the conducting of drying.

3.2 Effect of Freeze-thaw Placement Points and Times on the Quality of Tilapia Fillets

Figure 2 shows the effect of freeze-thaw placement points and times on the quality of tilapia fillets.

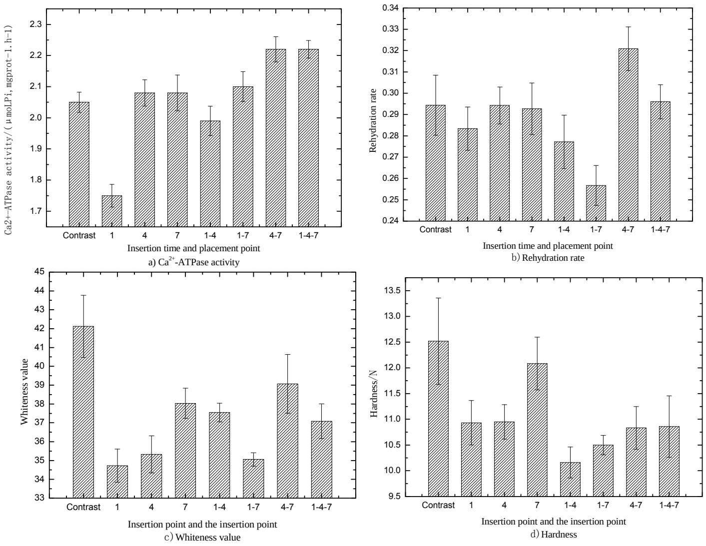

Figure 2: Effect of placement points and times of freeze-thawing process on quality of the dried-tilapia fillets

Figure 2(a) shows, in the condition of single freeze-thaw placement, the later placement time is, the higher activity of Ca^{2+}-ATPase. The activity of Ca^{2+}-ATPase reached the minimum value when placement point was set at 1st hour. There was no significant difference between placement points at 4th and the 7th hours. This was consistent with the same results of two times cycles of freeze-thaw placement. The Ca^{2+}-ATPase activity was no longer increased when three times of freeze-thaw placed into drying process. Perhaps in the 1st hour, drying didn't cause substantial damage to the protein because of low level of temperature of fish itself after freeze-thaw pretreatment and higher free water content within the fillets. But the placement at this point, the drying time didn't shorten and the Ca^{2+}-ATPase activity didn't achieve protection, either. On the other hand, the structure of the protein could be destroyed under inappropriate freeze conditions (Grimi et al, 2010), leading to lower enzyme activity. Therefore, the Ca^{2+}-ATPase activity of placement at 1st hour significantly declined compared with that of the control group. The placement point at intermediate level moisture was significantly better than that at a highwater content for the Ca^{2+}-ATPase activity.

Figure 2(b) shows, rehydration rate increased with the placement time delay in the condition of single freeze-thaw placement, but it was lower than the control group. The difference of rehydration rate between placement at 4th and 7th hours was just 0.54%. For the drying experimental group 1-7 and 1-4 that contained two times of freeze-thaw cycle, the rehydration rate reached the lowest value in 1-7. Whereas, the value reached highest in 4-7. Dehydration treatment can prevent cell rupture during freezing. After a period of pre-drying before freeze-thaw, structural damage would decrease to a lesser extent, and rehydration rate increased to the extent that was higher than the control group.

Figure 2(c) shows, the whiteness was increased with the placement time delay in the condition of single freeze-thaw placement. For two placement times, the whiteness of the 4-7 group samples was significantly higher than the other groups. As to three placement times, the whiteness decreased because of longer drying time. The whiteness values of all placement groups were lower than the control group. The whiteness increased with the delay of placement point in the single freeze-thaw placement group because pre-dehydration treatment had the ability to slow down the extent of cells cracking caused by freeze-thaw. The 1-7 test group samples were darker than 1-4. That was because freeze-thaw treatment carried out under initial high moisture content led to higher drip loss, and in the subsequent of drying process because of former long continuous thermal drying time, browning reaction was severe and persistent, whiteness decreased.

Figure 2(d) shows the effect of freeze-thaw placement points and times on the hardness. The control group had the highest hardness. For single placement times, it had no significant impact on the hardness for placement at 1th and 4th. As to the placement at 7th hour, the hardness was significantly higher than other

groups. The structure of fish fillet would be damaged to a certain extent because of freeze and thus caused fiber fracture (Liu et al, 2012). The impact of freezing was obvious when freeze-thaw process placed into drying at a higher moisture content. And placement under the condition of low moisture content, due to the sudden less water, freeze had no impact on organizational structure and dense dry hard state was obviously manifested owing to long time drying. Samples had a minimum hardness of 10.2 N when placement points were at 1st and 4th hours. The hardness of the test samples 1-4-7 was close to that of tests 1, 4 and 4-7.
The comprehensive scores using Comprehensively Weighted Grading Method for the samples that had different placement points and times are shown in table2. It shows that the comprehensive score reached maximum of 97.324 for test 4-7. The value increased 6.4% compared to the control group (91.485).

Table2: Effect of placement points and times of freeze-thaw process on the comprehensive scores of the dried-tilapia fillets (a -constrast)

Project and score								
Project	a	1	4	7	1-4	1-7	4-7	1-4-7
scores	91.48537	85.274	90.92118	90.36971	90.62308	88.40657	97.32337	93.99586

3.3 Optimization test for freeze-thaw process at 7th hour
While at 4th hour of drying, the moisture content decreased to moderate content. According to the completed test results at 4th hour of drying: freezing temperature and time is -40 °C and 1.5 h, melting temperature and time is 25 °C and 1.0 h, this freezing temperature is lower than that of freeze-thaw pretreatment. At the same time, the freezing time is increased and the melting time is reduced. When drying at 7th hour, the moisture content of the sample would be in a lower state. So the level of each factor must be appropriately adjusted to in the optimization process. Taking into account of energy consumption and operability in the actual production, the other indicators slightly modified other than the range of the freezing temperature. The three factors and three levels orthogonal test was conducted at 7th of drying freezing time, freezing temperature and melting time which work as factors. The design and analysis of result are shown in Table 3.

Table 3: The L_9 (3^4) orthogonal experiment and result for freeze-thaw placement at 7^{th} h

Test No.	Factor			Ca^{2+}-ATPase Enzyme activity	Rehydration rate	Whiteness value	Hardness /N	Comprehen-sive score
	A/Frozen temperature /°C	B/Frozen time/h	C/Melting time/h					
1	-20	1	0.5	2.01	28.85%	36.39	11.5	82.63
2	-20	1.5	1	2.14	29.51%	39.86	10.8	87.47
3	-20	2	1.5	2.06	27.43%	39.60	11.1	84.15
4	-30	1	1	2.10	29.71%	37.44	10.0	87.43
5	-30	1.5	1.5	2.65	30.95%	39.01	9.9	95.52
6	-30	2	0.5	2.73	34.32%	38.97	10.0	96.94
7	-40	1	1.5	2.14	28.57%	38.43	10.9	85.70
8	-40	1.5	0.5	1.91	29.49%	39.74	10.0	86.34
9	-40	2	1	2.65	29.90%	33.90	11.3	89.62
*K*1	84.750	85.253	89.413					
*K*2	93.990	89.693	88.173					
*K*3	87.220	91.013	88.373					
R	9.240	5.760	1.240					

According to Table 3, $A_2B_3C_1$ is the best result for freeze-thaw treatment process by the visual analysis, namely freezing temperature -30 °C, freezing time 2.0 h, melting time 0.5 h. The overall score reached the maximum value of 99.27 in this condition. The results of indexes are Ca^{2+}-ATPase activity 2.75, rehydration rate 34.32%, whiteness value 38.87, hardness 10 N. The order of various factors is A> B> C. In addition, significant analysis shows the result of variance analysis that freezing temperature and freezing time have great influence on the result, while melting time not on the impact of indicators.
Meanwhile, the corresponding results of the control group are: Ca^{2+}-ATPase activity 2.05, rehydration rate 29.44%, hardness values 12.5 N and whiteness values 42.12, comprehensive score 85.071. The indicators in the optimum process had a greater degree of improvement and the comprehensive score increased by 17%.
To analyze the condition of each freeze-thaw placement in the entire process, the time required for freezing was increased with the process of drying while the melting time was reduced with the drying process. It was

perhaps in the reason of the content of free water decreased and the proportion of bound water that is difficult to remove increased, combined with half-bound water and bound water released into free water owing to freeze that needed enough freezing time.

4. Conclusions

The law of drying process and the drying rate curves under various states that freeze-thaw placed at different points of the heat pump drying were obtained. Freeze-thaw could contribute to the drying rate in short time. But it was weakened with the drying process and placement point delay. The twice freeze-thaw cycles process at 4^{th} and 7^{th} hours of drying can effectively improve the quality of the dried product.
The optimum condition for freeze-thaw cycles combined with heat pump drying of tilapia fillets are obtained through twice optimization tests at 4th and 7th hours for freeze-thaw placement. As follows: freeze-thaw pretreatment (freezing conditions: -32°C, 1.0h; melting conditions: 20°C, 1.0h), heat pump drying 4h (temperature 45 °C, air speed 2.5 m/s, humidity 30%), freeze-thaw placement (freezing conditions: -40°C, 1.5h; melting conditions: 25°C, 1.0h), heat pump drying 3h (same conditions as before), freeze-thaw placement (freezing conditions: -30°C, 2.0h; melting conditions:25°C, 0.5h), heat pump drying to 0.30±0.02 for the dry basis moisture content., the Ca^{2+}-ATPase activity, rehydration rate, whiteness and hardness are 2.75 μmolPi /mgprot/h, 34.32%, 38.87 and 10.0 N, respectively. Meanwhile, the comprehensive score is 99.27 which is increased by 17% compared to the control group.

Acknowledgments

The authors acknowledge the financial support from the Natural Science Foundation of Guangdong Province with grant No. 2015A030313613, The Science and Technology Department Project of Guangdong Province with grant No. 2014A020208115, Project of Enhancing School With Innovation of Guangdong Ocean University No. 2014KTSCX076.

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