

## Quality enrichment and preservation of shrimp by fortification with fishes and flours employing fast vacuum-drying

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### Abstract

Shrimp (*Metapenaeus monoceros*) is low in fat, essential minerals and vitamins. It contains high moisture ( $77.15 \pm 0.73\%$ ), so it needs to be preserved by an energy-efficient process. Therefore, fortification protocols for the enrichment of shrimp were developed employing two fishes namely *Catla catla* (CA) and *Chela cachius* (CS). Pre-sterilised shrimps were blended with sterilised CA and CS at 2:1:1 weight ratio. Pre-blended shrimps were converted to fortified shrimp (FS) by adding corn, rice flour (FS-1) and additionally mixing with dried-ginger (FS-2) and subsequently dehydrated by vacuum-drying (VD) using silver/copper plated multidimensional heater to produce vacuum-dried FS. The VD kinetics indicated faster dehydration of FS-1 as compared to FS-2 in both heaters. Higher effective diffusivity ( $7.464 \times 10^{-10} \text{ m}^2/\text{s}$ ) and lower activation energy (28.42 kJ/mol) were computed for FS-1 in silver plated heater. The vacuum-dried FS-1 exhibited superior quality through remarkable augmentation in protein (188%),  $\omega$ -3 fatty acids (20%), carbohydrate (35%), ash (151%) and other essential elements with acceptable water activity, rehydration ratio, TVBN and histamine content.

### Abbreviation list

CA: catla fish (*Catla catla*); CS: chela fish (*Chela cachius*); CPMDH: copper-plated multidimensional heater; CF: corn flour; CHD: coronary heart disease; DSC: differential scanning calorimetry; DG: dried ginger; FS-1: fortified shrimp and blended set-1; FS-2: fortified shrimp and blended set-2; MR: moisture ratio; RR: rehydration ratio; RTD: resistance temperature detector; RF: rice flour; SPMDH: silver-plated multidimensional heater; STSP: shrimp-CA-CS pulp; SBM: sterilised brine mix; TVBN: total volatile base nitrogen; VD: vacuum-drying; VDFS-1: vacuum-dried fortified shrimp and blended set-1; VDFS-2: vacuum-dried fortified shrimp and blended set-1.

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### Introduction

Shrimp (*Metapenaeus monoceros*) is considered a tasty and healthy foodstuff worldwide. Though it is costly, it is a rich source of protein, energy, minerals (Fe, I, Se, Mg, Na, Mn, Cu, S), pigments (astaxanthin and astacin), and vitamin E (Bogard *et al.*, 2015). However, it is low in fat, Zn, Ca, P, K, and vitamins A, B<sub>12</sub> and D (Bogard *et al.*, 2015). So, it needs to be enriched using other foodstuffs to overcome these deficiencies. The presence of high moisture (77.15

$\pm 0.73\%$ ) in shrimp also enhances its deterioration, thereby reducing its shelf-life. Shrimp preservation is thus needed to extend its shelf-life. Therefore, the enrichment of nutrients through fortification and successive reduction of moisture content through energy-efficient drying for preservation of fortified shrimp are very important.

Coronary heart disease (CHD) is a major killer in both developed and developing countries. CHD is also dangerous due to its sudden attack. In Japan, the low death rate from CHD is reported since the

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consumption of fish (rich in  $\omega$ -3 PUFA) is estimated to be about 100 g/day (Kromhout *et al.*, 1985). Hence, to reduce the risk of CHD, the recommended intake of fish is two to three servings per week (Sen, 2005).

The tropical fish such as catla (*Catla catla*) [CA] contains a high amount of K, protein and fat/ $\omega$ -3 fatty acids (Vanitha, 2011; Bogard *et al.*, 2015; Mohanty *et al.*, 2016). Vanitha (2011) has developed value-added products from CA. Another tropical fish, chela (*Chela cachius*) [CS], is rich in Zn, Ca, P, Mn, S, and vitamins A, D and B<sub>12</sub> (Bogard *et al.*, 2015). Small indigenous fish species like CS has been used for contributing dietary vitamin A, Ca and Fe in total household fish consumption (Roos *et al.*, 2003). Therefore, the deficiency in shrimp can be mitigated by fortification with CA and CS at specific proportions.

Rice flour (RF) functions as a thickening agent, and texture and flavor improver (Duncan, 2000), while corn flour (CF) is rich in carbohydrate, essential elements (Fe, Ca, Cu, K, P, Zn), and vitamins [thiamine, niacin, vitamin B<sub>6</sub>] (Sabanis and Tzia, 2009). Jaya Shankar and Bandyopadhyay (2005) previously blended RF with fish powder through an extrusion process. Sabanis and Tzia (2009) used CF along with RF and soy flour to improve bread characteristics. Dried ginger powder (DG) contains a high quantity of  $\beta$ -ionone [anticancer agent] (Liu *et al.*, 2008). It has been used as taste and flavor enhancer (Sangwan *et al.*, 2014), and is also rich in ash and Ca (Kirk and Sawyer, 1991).

Chakraborty and Samanta (2015) reported an application of vacuum-drying (VD) for producing highly nutritious foodstuffs by enriching alphonso mango with aloe vera (*Aloe barbadensis* Miller) blend. Almeida-Trasvina *et al.* (2014) optimised VD [pressure (46.33 kPa, abs) and temperature (68.33°C)] to preserve antioxidants present in apple pomace, and Alibas (2012) investigated the drying of celeriac slices using VD by different reduced pressures (0.1, 3, 7, 10, 13 and 17 kPa) and temperatures (55, 65 and 75°C). Recently, fish powders were produced for the fortification of biscuits (Mohamed *et al.*, 2014), bread (Adeleke and Odedeji, 2010) and ice-cream (Shaviklo *et al.*, 2011). Fish oils (Kolanowski and Laufenberg, 2006) contain  $\omega$ -3 fatty acids, and related products such as microencapsulated fish-oil (Serfert *et al.*, 2010) had been used for the preparation of different foodstuffs.

From the literature, however, it is evident that enrichment of shrimp with fish (CA and CS) has not been reported till date. Accordingly, in the present work, shrimp has been fortified by blending with two different fishes (CA, CS) for improvement in nutritional qualities. Moreover, RF, CF, and DG have

also been amalgamated with pre-fortified shrimp for further improvement in overall quality. To improve the shelf-life, the fortified shrimp was vacuum-dried using novel silver-plated multidimensional heater (SPMDH) or copper-plated multidimensional heater (CPMDH) to enhance the drying operation. The final qualities of dried products were assessed using standard protocols.

## Materials and methods

### Sampling protocol

Shrimp, CA and CS were collected from the local market (Haldia, India) and were cleaned with deionised water. After scraping off the scales and gills, CA and CS were gutted using a sterilised knife. CA and CS were then filleted. Shrimps were de-headed, de-tailed and de-veined to obtain the flesh. After cleaning with deionised water, shrimp was stored along with CA and CS in polyethylene bags (51  $\mu$ m) under refrigeration (5 - 8°C).

### Sample sterilisation

Shrimp, CA and CS were taken at weight ratio of shrimp:CA:CS 2:1:1, and immersed into 1.5% (w/v) brine solution kept in a 250 mL stainless steel container (with lid) for sterilisation (at 121°C, 15 psi, 15 min). The moisture [Test Method: IS 1158: 1973 (RA-2010)] and pH (determined by calibrated pH meter: SYSTRONICS, Ahmedabad, India, serial no.7743) of brine solution (1.5%), raw and sterilised shrimp (along with CA and CS) were measured. The whole part of sterilised brine mix (SBM) was used further in the subsequent blending step to prevent nutrient loss from the samples. The pH of SBM was measured by the same instrument.

### Fortification of shrimp

The sterilised shrimp along with sterilised CA and CS were blended using a blender (PHILIPS, model no. HL 1632, 230 V, AC, 50 Hz, 500 W) to obtain shrimp-CA-CS pulp (STSP). Subsequently, STSP and SBM were further enriched by mixing with CF and RF at STSP:CF:RF ratio of 2:0.2:0.04 in the same blender by "step wise-short time (20 s to 30 s) addition and mixing methodology". The blending was performed at moderate speed (~400 - 500 rpm) to avoid development of unwanted reaction(s), unpleasant flavours and tastes during preparation of fortified shrimp and blended set-1 (FS-1). Similarly, fortified shrimp and blended set-2 (FS-2) was prepared through the addition of CF, RF and DG to the STSP and SBM at a STSP:CF:RF:DG ratio of 2:0.2:0.04:0.02. The final moisture content and pH

Table 1. Parts (weight basis) of shrimp, CA, CS, STSP, SBM, RF, CF and DG for preparations of FS-1 and FS-2 samples by successive sterilisation, fortification and blending steps.

Fortified shrimp and blended product	Shrimp (sterilised)	CA (sterilised)	CS (sterilised)	Shrimp-CA-CS pulp (STSP)	SBM [1.5% (w/v) brine solution]	Added part to STSP		
						RF	CF	DG
FS-1	2 parts	1 part	1 part	4 parts	whole part (50 mL)	0.4	0.08	-
FS-2	2 parts	1 part	1 part			0.4	0.08	0.04

of both FS-1 and FS-2 were determined. The details of FS-1 and FS-2 preparation are shown in Table 1.

#### Vacuum-drying (VD) of FS-1 and FS-2

The prepared FS-1 and FS-2 were weighed (approximately  $25 \pm 0.01$  g of a batch) and placed on SPMDH or CPMDH (depth or thickness of sample 0.002 m) and subjected to VD (0.5 Pa vacuum pressure, condenser temperature  $-40^\circ\text{C}$ ). Self-designed and fabricated cuboid ( $120 \times 120 \times 90$  mm) heater (220 V, 166 mA, 36 W) viz. SPMDH or CPMDH in which the heat was supplied from four sides metallic (stainless steel) walls and bottom; top of the heater was kept open for diffusion of water-vapour from FS-1/FS-2. One resistance temperature detector (RTD) was used for measuring the temperature of the inside wall (stainless steel) and it was connected with the PID controller. The inside wall temperature was set at  $55^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ ). Another RTD was inserted into FS-1/FS-2 for measuring the VD sample's temperature over 40 to  $50^\circ\text{C}$ . The weight of the sample undergoing VD was recorded at fixed time interval (15 min) for evaluation of drying kinetics. The VD was continued till the final moisture content of the sample became  $\approx 3\%$  (w/w). The final VD products were marked as VDFS-1 and VDFS-2, corresponding to the FS-1 and FS-2, respectively.

#### Drying kinetics

Seven drying models namely Newton, Page, Henderson and Pebis, Modified Page, Linear, Wang and Singh, and Modified Wang and Singh were implemented to assess the best representative drying kinetics during VD (Dongbang and Pirompugd, 2015; Fernando and Amarasinghe, 2016; Chakraborty and Samanta, 2017). The selected mathematical models and their equations are shown in Table 2.

The regression coefficient [ $R^2$ ], root mean square error [RMSE], Chi-square [ $\chi^2$ ] and mean relative deviation [E%] have been evaluated to determine the 'goodness of fit' of the selected models for both FS-1 and FS-2 employing SPMDH and CPMDH. The diffusion equation (unsteady state) for the calculation of effective diffusion coefficient ( $D_{\text{eff}}$ ) is given as reported by Taheri-Garavand and Meda (2018):

$$MR = \frac{8}{\pi^2} \text{Exp} \left[ -\frac{\pi^2 * D_{\text{eff}} * t}{4L^2} \right] \quad (\text{Eq. 1})$$

where,  $MR$  = moisture ratio,  $t$  = time in seconds,  $L$  = thickness or depth of sample in SPMDH or CPMDH.  $R^2$  was evaluated by Microsoft Excel 2010, while RMSE and  $\chi^2$  were calculated by the following equations (Chakraborty and Roychowdhury, 2013):

Table 2. Mathematical models selected and statistical data ( $R^2$ , RMSE,  $\chi^2$ , E%) for two sets of fish samples (FS-1 and FS-2) using SPMDH and CPMDH.

Model	Equation	SET	SPMDH				CPMDH			
			$R^2$	RMSE	$\chi^2$	E (%)	$R^2$	RMSE	$\chi^2$	E (%)
Newton	$MR = \exp(-Kt)$	FS-1	0.938	0.109	0.013	8.21	0.928	0.091	0.009	8.76
		FS-2	0.901	0.199	0.046	14.49	0.974	0.052	0.003	18.74
Page	$MR = \exp(-Kt^n)$	FS-1	0.978	0.051	0.004	5.96	0.893	0.159	0.035	13.79
		FS-2	0.989	0.052	0.004	2.30	0.995	0.069	0.007	35.23
Henderson and Pabis	$MR = A \exp(-Kt)$	FS-1	0.918	0.225	0.067	37.81	0.863	0.138	0.026	23.34
		FS-2	0.890	0.966	0.186	35.16	0.939	1.069	0.229	29.48
Modified Page	$MR = \exp[-(Kt)^n]$	FS-1	0.986	0.074	0.007	26.21	0.981	0.033	0.001	25.14
		FS-2	0.989	0.051	0.004	2.29	0.854	2.172	6.605	25.58
Linear	$MR = A + Bt$	FS-1	1.000	0.044	0.003	7.65	1.000	0.069	0.007	22.31
		FS-2	1.000	0.049	0.003	16.17	1.000	0.049	0.003	23.09
Wang and Singh	$MR = 1 + At + Bt^2$	FS-1	0.996	0.128	0.022	23.49	1.000	0.067	0.006	27.51
		FS-2	0.994	0.055	0.004	4.28	0.997	0.046	0.001	36.03
Modified Wang and Singh	$MR = (1 + At + Bt^2) / (1 + Ct)$	FS-1	0.989	0.068	0.007	21.88	0.999	0.055	0.005	26.41
		FS-2	0.949	0.281	0.019	9.28	0.998	0.136	0.005	41.67

$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^N (MR_{pre,i} - MR_{exp,i})^2 \right]^{0.5} \quad (\text{Eq. 2})$$

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{exp,i} - MR_{pre,i})^2}{N - p} \quad (\text{Eq. 3})$$

where,  $MR_{pre,i}$  = predicted moisture ratio,  $MR_{exp,i}$  = experimental moisture ratio,  $N$  = number of observations, and  $p$  = number of constants.

#### Mean relative deviation (E%)

Absolute value, which provides a clear idea of the mean divergence of the predicted data from the experimental data, was used in the present work to examine the 'goodness of fit'. Value of  $E\% < 5$  indicates an 'extremely good fit', 5 to 10% 'reasonably good fit', and  $> 10\%$  shows 'poor fit' (Lomauro *et al.*, 1985; Gencturk *et al.*, 1986). The formula to calculate the mean relative deviation is as follows:

$$E\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{(MR_{exp,i} - MR_{pre,i})}{MR_{exp,i}} \right| \quad (\text{Eq. 4})$$

Table 3. pH and moisture of fish samples at different stages of processing before and after vacuum-drying (VD).

pH and Moisture	CA		CS		Shrimp		STSP	SBM	FS-1	FS-2	VDFS-1	VDFS-2
	Raw	Sterilised	Raw	Sterilised	Raw	Sterilised						
pH	5.88 ± 0.02	6.47 ± 0.03	5.80 ± 0.02	6.30 ± 0.03	6.40 ± 0.02	6.66 ± 0.02	6.32 ± 0.03	5.60 ± 0.03	5.90 ± 0.02	6.20 ± 0.03	6.63 ± 0.02	6.33 ± 0.02
Moisture (%)	78.11 ± 0.75	68.87 ± 0.66	74.81 ± 0.71	67.35 ± 0.64	77.15 ± 0.73	68.76 ± 0.65	69.12 ± 0.68	-	64.97 ± 0.62	64.34 ± 0.64	3.06 ± 0.25	3.06 ± 0.25

Data are means ± standard deviation. STSP: sterilised shrimp-CA-CS pulp; SBM: sterilised brine mix; FS: fortified shrimp and blended set; VDFS: vacuum-dried FS product.

Table 4. Proximate analysis and different elements present in VDFS-1 and VDFS-2 (using SPMDH).

Quality Parameter	Shrimp (raw)	VDFS-1	VDFS-2	Test method (s) / [Reference(s)]
Total Carbohydrate (g/100 g) ± SD*	0	34.99 ± 0.36	37.50 ± 0.34	AOAC 986.25 [FSSAI (2010)]
Protein (g/100 g) ± SD	17.6	50.66 ± 0.31	48.78 ± 0.28	IS: 7219 - 1973 [Chakraborty and Samanta (2015)]
Total Fat (g/100 g) ± SD	1	4.71 ± 0.05	4.73 ± 0.05	AOAC 963.15 [Chakraborty and Samanta (2015)]
Total ash (g/100 g) ± SD	2.2	5.52 ± 0.44	5.19 ± 0.42	IS: 1158 - 1973 [FSSAI (2010)]
Energy (kJ/100 g) ± SD	333	1609.26 ± 1.95	1642.28 ± 1.92	Pearson's composition and analysis of foods [FSSAI (2010)]
ω-3 fatty acids (g/100 g) ± SD	2.0	2.4 ± 0.03	2.2 ± 0.03	AOAC 996.06 [Kromhout <i>et al.</i> (1985)]
Histamine (mg %) ± SD	-	5 ± 0.01	5 ± 0.01	FSSAI Lab Manual 6 [Sen (2005)]
TVBN (mg/100 g)	-	Below detection limit (5.0)	Below detection limit (5.0)	FSSAI Lab Manual 6: Cl.no. 1.3 [Idakwo <i>et al.</i> (2016)]
Mercury (Hg) (mg/kg)	-	Below detection limit (0.01)	Below detection limit (0.01)	AOAC 971.21 [Torres-Escribano <i>et al.</i> (2010)]
Fe (mg) ± SD	2.70	5.92 ± 0.88	5.80 ± 0.86	AOAC (1999) [Yanar <i>et al.</i> (2004)]
Zn (mg) ± SD	1.30	4.68 ± 0.51	4.56 ± 0.52	AOAC (1999) [Yanar <i>et al.</i> (2004)]
Ca (mg) ± SD	550	1259.26 ± 0.11	1272.97 ± 0.10	AOAC (1999) [Yanar <i>et al.</i> (2004)]
P (mg) ± SD	290	864.22 ± 0.92	830.75 ± 0.91	AOAC (1999) [Yanar <i>et al.</i> (2004)]
K (mg) ± SD	210	528.69 ± 0.78	504.44 ± 0.81	AOAC (1999) [Yanar <i>et al.</i> (2004)]
Cu (mg) ± SD	0.49	0.8385 ± 0.42	0.6345 ± 0.52	AOAC (1999) [Yanar <i>et al.</i> (2004)]
Mg (mg) ± SD	45	93.77 ± 0.02	91.22 ± 0.02	AOAC (1999) [Yanar <i>et al.</i> (2004)]
S (mg) ± SD	190	458.22 ± 0.64	445.66 ± 0.62	AOAC (1999) [Yanar <i>et al.</i> (2004)]

SD: Standard deviation.

The relation between activation energy (E) and  $D_{\text{eff}}$  were calculated by the Arrhenius equation:

$$\ln \left( \frac{D_{\text{eff},2}}{D_{\text{eff},1}} \right) = \left( \frac{E}{R} \right) \left[ \frac{(T_2 - T_1)}{T_1 * T_2} \right] \quad (\text{Eq. 5})$$

#### Quality assessment

The moisture (%), pH, total carbohydrate, protein, total fat, energy, ash, essential elements (Fe, Zn, Ca, P, K, Cu, Mg, and S),  $\omega$ -3 fatty acid, TVBN, histamine and Hg content of the VDFS-1 and VDFS-2 were measured in triplicate, and the means and standard deviations (SD) were reported (Table 3 and Table 4).

#### Rehydration ratio (RR)

Rehydration ratio (RR) was also measured (Chakraborty *et al.*, 2011) for both VDFS-1 and VDFS-2. All the two sets of VD products were properly stored in airtight polythene containers and bag. After that, they were tested for rehydration ratio (RR). Briefly, 5 g sample of stored VD product was taken and dispersed in 100 mL distilled water at 60°C for 30 min. The solution of fish powder (product) and water were filtered by 0.4  $\mu\text{m}$  Whatman filter paper. The filtrate was discarded, and the precipitate was taken. The precipitate was blotted with tissue paper to remove excess water, and the weight of rehydrated sample of two sets (VDFS-1 and VDFS-2) was measured. The RR is expressed by the following equation:

$$RR = \left( \frac{W_{\text{reVDFS}}}{W_{\text{VDFS}}} \right) \quad (\text{Eq. 6})$$

where,  $W_{\text{VDFS}}$  = VDFS sample weight taken for testing (initial),  $W_{\text{reVDFS}}$  = VDFS sample weight (after rehydration).

#### Water activity ( $a_w$ ) and microbiological assay

Water activity ( $a_w$ ) is an indicator of the available free water (Ramaswamy and Marcotte, 2005). Food can be made safe to store by lowering the  $a_w$  to a point that does not allow pathogens such as *Clostridium botulinum* and *Staphylococcus aureus* to grow in it.  $a_w$  was measured by a water activity measurement instrument (Aqua Lab, CX-2). The microbiological assay was also performed for the identification/presence of bacteria and yeasts and moulds (Harrigan, 1998) in final dried products.

After six months, the refrigerated (5 - 8°C) products (VDFS-1 and VDFS-2) were assessed through  $a_w$  and microbiological assay to determine

the 'shelf-life' and 'antimicrobial activity'. For both products, the  $a_w$  data were measured in triplicate, and reported as means and SD.

#### Differential scanning calorimetry

Calorimetry is the basic technique by which a relationship is drawn between the temperature and specific physical properties of the considered substance. The protein molecules and their complexes are formed by the thermodynamically driven reactions. The supersensitive calorimetric techniques such as differential scanning calorimetry (DSC) is used to determine the thermal stability of proteins. From the endothermic heat flow (mW) vs. temperature (°C) plot, exhibition of multiple transition peaks denotes the denaturation of protein. Accordingly, DSC (Pyris Diamond DSC, Perkin Elmer Co., USA) was performed (from 10 to 100°C) for VDFS-1 and VDFS-2 to assess their thermal stability.

## Results and discussion

#### pH and moisture analysis of shrimp and fishes before and after vacuum-drying

From Table 3, it was found that after sterilisation, the pH levels of shrimp, CA and CS had increased. The pH of SBM decreased to  $5.60 \pm 0.03$  from  $6.90 \pm 0.03$  (1.5%, w/v, brine solution). It was suggested that the basic  $\text{Na}^+$  ions present in brine solution were partly transferred to all sterilised samples.

After blending with SBM, CF, RF, with or without DG, the moisture content of the two fortified samples (FS-1 and FS-2) dropped, implying that the addition of CF, RF, and DG helped gaining nutrition while reducing the moisture of STSP. The final vacuum-dried products (VDFS-1 and VDFS-2) were found to contain  $3.06 \pm 0.25\%$  moisture (wet basis). The alkalinity of VDFS sample(s) increased; thus making the products "alkaline food". This happened due to more ion diffusivity into dried samples owing to reverse water removal (Sarkar and Tirumkudulu, 2009). In comparison with raw shrimp (pH =  $6.40 \pm 0.02$ ), the pH of VDFS-1 was determined to be higher ( $6.63 \pm 0.02$ ) and VDFS-2 was lower ( $6.33 \pm 0.02$ ).

#### Vacuum-drying kinetics, models and drying time

The VD model constants (K, A, B, C, n), for seven model equations (Table 2) for both the products FS-1 and FS-2 (using the corresponding heater) were computed using experimental data. The variation of experimental MR with VD time is shown in Figure 1(A) and Figure 1(B) for FS-1, FS-2, respectively, using both SPMDH and CPMDH.

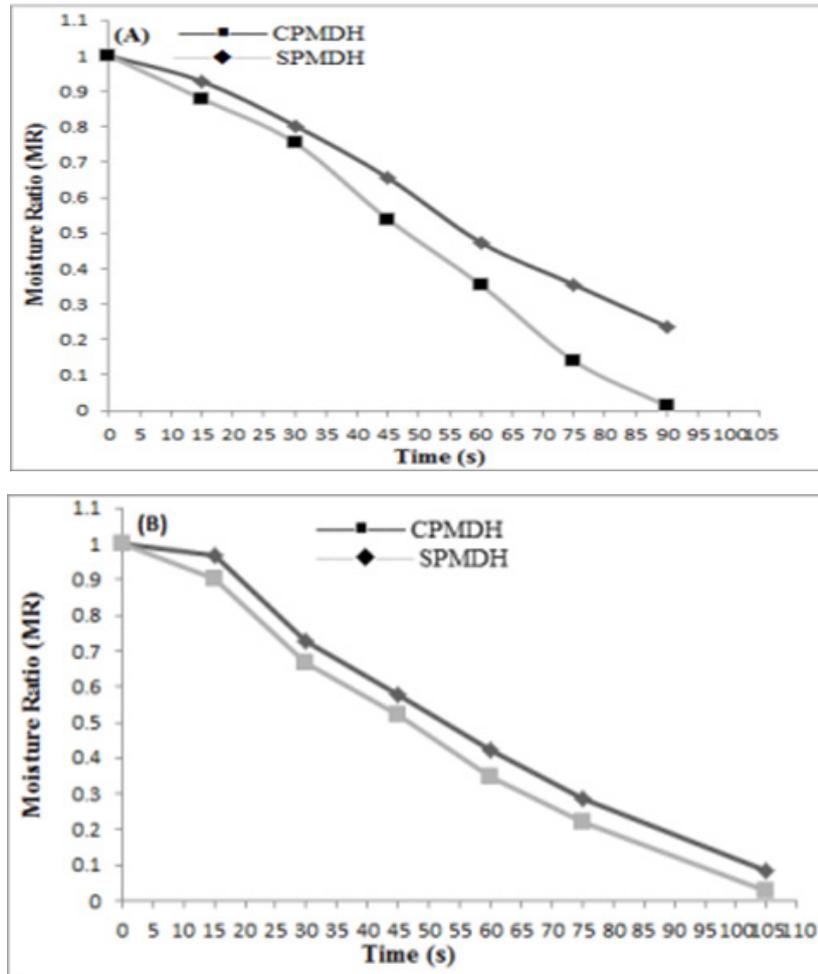


Figure 1. Moisture ratio (MR) vs. time for (A) vacuum-drying of FS-1 sample using SPMDH and CPMDH, and (B) vacuum-drying of FS-2 sample using SPMDH and CPMDH.

For FS-1, the VD time was found less for both SPMDH [2.55 h] and CPMDH [2.85 h] in comparison with FS-2 [3.25 h and 3.76 h by using SPMDH and CPMDH, respectively]. The probable reason might be the enhanced internal resistance to moisture diffusion during VD for FS-2 than FS-1, since DG (1%, w/w) was additionally added to FS-2 only. That means addition of DG had a significant adverse effect on VD time.

#### Statistical analysis of VD models

The numerical values of  $R^2$  (Microsoft Excel 2010), RMSE,  $\chi^2$ , and  $E\%$  values as expressed by equations (2), (3), and (4), respectively pertaining to the vacuum-drying (VD) models for both FS-1 and FS-2 (using corresponding SPMDH and CPMDH) were calculated to know the best fitting/accepted model out of seven models, and are presented in Table 2. Highest  $R^2$ , lowest values of RMSE, as well as  $\chi^2$  and  $E\%$  ( $< 5$ ) values were computed and found in Linear (using SPMDH) and Modified Page (using CPMDH) models in VD of FS-1, while similar results

were determined in Modified Page (using SPMDH) and Newton (using CPMDH) models in VD of FS-2. Accordingly, these models were considered the best representative of the VD kinetics.

#### Effective diffusivity ( $D_{eff}$ ) and activation energy ( $E$ )

The  $D_{eff}$  in VD of FS-1 and FS-2 under SPMDH and CPMDH over a temperature range from 40°C to 50°C were calculated using equations (1) and (5). At 50°C, by using SPMDH for FS-1, the  $D_{eff}$  value was found higher ( $7.464 \times 10^{-10} \text{ m}^2/\text{s}$ ) than FS-2 ( $D_{eff} = 6.366 \times 10^{-10} \text{ m}^2/\text{s}$ ). In the case of CPMDH (at 50°C), the  $D_{eff}$  values were found lower for both FS-1 and FS-2 as compared to SPMDH. The activation energy ( $E$ ) required for VD for FS-1 and FS-2 (using SPMDH) were 28.42 and 37.38 kJ/mol, respectively which were much lower than 43.09 and 55.59 kJ/mol for FS-1 and FS-2 (using CPMDH), respectively. Thus, SPMDH was observed to be more energy efficient than CPMDH.

As SPMDH rendered higher drying rate in comparison with CPMDH; beside SPMDH

possessing higher antimicrobial efficacy; hence, both the final products (VDFS-1 and VDFS-2) were developed using SPMDH and subsequently tested for quality assessments.

#### Rehydration ratio (RR)

By using equation (6), the results of RR were found to be  $2.68 \pm 0.03$  and  $2.50 \pm 0.03$  for VDFS-1 and VDFS-2, respectively. This suggested that VDFS-1 had more RR than VDFS-2. Chakraborty *et al.* (2011) reported a RR value of 2.41 for infrared-assisted freeze-dried tiger prawn product, which was lower as compared to both VDFS products reported in the present work.

#### Water activity ( $a_w$ ) and microbiological assay

The  $a_w$  was determined as  $0.228 \pm 0.005$  and  $0.196 \pm 0.005$  for VDFS-1 and VDFS-2, respectively. As per FSSAI (2010) guidelines, the  $a_w$  of any finished fish products must be  $< 0.78$ ; the  $a_w$  values of both VDFS products were notably less than the FSSAI limit, thus conforming to the market status. Low  $a_w$  values for both the final products suggested that they possessed acceptable shelf-life and stability. It may further be observed that VDFS-2 had longer shelf-life and higher antimicrobial activity than VDFS-1.

#### Quality assessment

The results of the proximate analysis of VDFS-1 and VDFS-2 (100 g each) are shown in Table 4.

#### Total carbohydrate, protein, total fat, total ash

For VDFS-2, the increment in carbohydrate content was found over VDFS-1. In comparison with raw shrimp sample, VDFS-2 had 37.5 units more than raw shrimp; whereas VDFS-1 had 35 units more carbohydrate content since DG was added for FS-2 making.

The protein content was  $50.66 \pm 0.31$  g and  $48.78 \text{ g} \pm 0.28/100$  g for VDFS-1 and VDFS-2, respectively. Thus, protein content increment in VDFS-1 and VDFS-2 were 188% and 177%, respectively as compared to raw shrimp (17.6 g/100 g).

The total fat content of the two products was found almost the same [ $4.71 \pm 0.05$  g (VDFS-1) and  $4.73 \pm 0.05$  g (VDFS-2)/100 g] since they were made of almost similar compositions except for DG in VDFS-2. The fat content increased almost five times in comparison with that of raw shrimp (1 g/100 g). Abraha *et al.* (2017) found 3.74 g fat per 100 g dried anchovy fish, which was well below the fat content of two VDFS products.

The total ash content for VDFS-1 and VDFS-2 was  $5.52 \pm 0.44$  g and  $5.19 \pm 0.42$  g per 100 g dried

products, respectively. For both the products, the total ash content increased about 2 to 2.5 times as compared to raw shrimp (2.2 g/100 g). Thus, 151% increment in total mineral content was achieved in VDFS-1 which was higher than the increment in VDFS-2 (136%). Shaviklo (2015) reported 1.60 g ash per 100 g freeze-dried tilapia fish, and 2.08 g ash per 100 g spray-dried tuna fish, both of which were lower as compared to the ash content of the VDFS products assessed in the present work.

#### Essential elements

For end products, eight essential elements namely Fe, Zn, Ca, P, K, Cu, Mg, and S were measured and compared with those of raw shrimp. Abbey *et al.* (2016) measured the Cu, Zn and Ca content as 0.25 mg, 1.88 mg and 1066.5 mg, respectively per 100 g dried tuna fish powder. Thus, the developed VDFS products contained higher concentration of elements (Cu, Zn and Ca) than dried tuna fish powder. It was found that increments of those elements were greater for VDFS-1 than VDFS-2 except for Ca. For VDFS-1, the increments were 119%, 260%, 129%, 198%, 152%, 71%, 108% and 141% for Fe, Zn, Ca, P, K, Cu, Mg and S, respectively (Table 4) as compared to those in raw shrimp.

#### Energy

The energy content was almost equal at 1609.26  $\pm 1.95$  kJ and  $1642.28 \pm 1.92$  kJ/100 g for VDFS-1 and VDFS-2, respectively which were much higher as compared to 333 kJ, 267 kJ and 349 kJ per 100 g raw shrimp, CA and CS, respectively. Marginal difference in energy content (about 33 kJ/100 g) between VDFS-1 and VDFS-2 could be due to the addition of DG to FS-2. Abbey *et al.* (2016) found less energy content (1333 kJ/100 g) in dried tuna fish powder as compared to the two VDFS products assessed in the present work.

#### $\omega$ -3 fatty acids

The  $\omega$ -3 fatty acids were measured around  $2.4 \pm 0.03$  for VDFS-1 and  $2.2 \pm 0.03$  g/100 g for VDFS-2, which were significantly greater than (0.55 g/100 g) that of dried anchovy (*Stelophorus heterolobus*) (Abraha *et al.*, 2017). According to Kris-Etherton *et al.* (2002), the intake of  $\omega$ -3 PUFA is preferable from dietary approach; since the consumption of 1 g per day  $\omega$ -3 fatty acids is beneficial to reduce cardiovascular disease, stroke (cerebral infarctions) and there is no risk of side effects (gastrointestinal disturbances and nausea) through its ingestion. As compared to raw shrimp ( $\omega$ -3: 2.0 g/100 g); about 20% increment in  $\omega$ -3 fatty acids could be achieved.

### Histamine and total volatile base nitrogen (TVBN)

For both VDFS-1 and VDFS-2, the histamine content was  $5 \pm 0.01$  mg%. The regulatory limit for histamine by the USA is 20 mg% (lowest among all countries). Therefore, the histamine content of the prepared foodstuffs was found well below the permissible limit. Hwang *et al.* (2012) estimated histamine in dried milkfish (*Chanos chanos*) in the range of 117.3 - 382.1 mg/100 g dried fish, which was well above the histamine value found in the present work.

In both end products, TVBN was found below the detection limit (detection limit: 5 mg/100 g); thus, indicating acceptability for human consumption; since TVBN was much lower than the threshold 40 mg N per 100 g sample. Notably, de Koning (2002) reported TVBN level (for several fish meals) over the range from 85 to 170 mg/100 g dried fish meal which was considerably higher than the present data. Abraha *et al.* (2017) also found greater TVBN content ( $20.12 \pm 0.20$  mg/100 g) in dried anchovy (*Stelophorus heterolobus*) as compared to both VDFS-1 and VDFS-2 assessed in the present work.

### Mercury (Hg)

The joint Food and Agriculture Organization (FAO) and World Health Organization (WHO) recommended 5  $\mu$ g/kg body weight per week (daily intake 0.71  $\mu$ g Hg/kg body weight) maximum level of Hg consumption (Torres-Escribano *et al.*, 2010). In both product samples, Hg was found below the detection limit (0.01 mg/kg). Therefore, it was safe to consume both the fortified shrimp products. Panichev and Panicheva (2016) reported Hg content for 14 different processed fishes that ranged from 135 ng/g (0.135 mg/kg) to 666 ng/g (0.666 mg/kg); evidently, these were much higher than that found in the present work.

### DSC

In Figure 2(A) (VDFS-1), no protein denaturation was found since the profile was found very smooth up to 100°C. On the contrary, in Figure 2(B) (VDFS-2), many transition peaks were observed (around 50 and 65°C) over the temperature range from 10°C to 100°C indicating thermal degradation. For VDFS-2, the rapid increment in endothermic heat flow

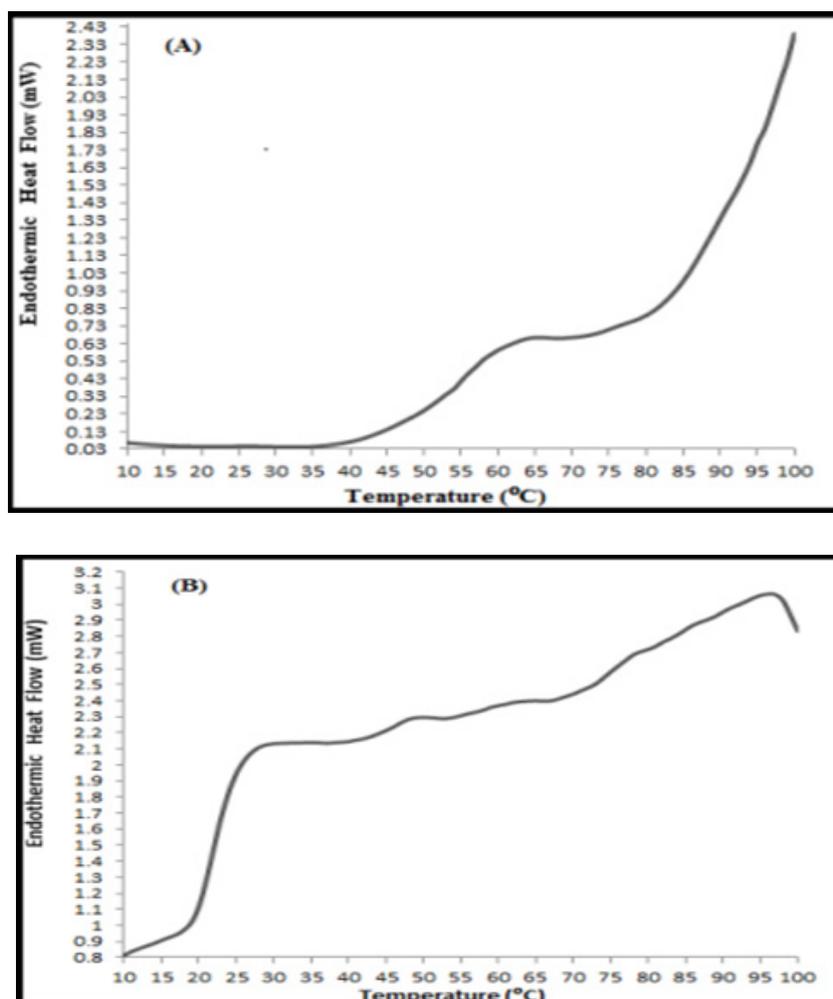


Figure 2. DSC thermogram of (A) VDFS-1, and (B) VDFS-2.

was possibly due to the presence of DG having higher specific heat (1.92 kJ/kg/ K). Hence, VDFS-1 demonstrated higher thermal stability as compared to VDFS-2. Besides, the higher glass transition temperature of VDFS-1 ( $T_g = 54.57^\circ\text{C}$ ) than VDFS-2 ( $T_g = 22.02^\circ\text{C}$ ) implied its superior thermal stability. Moreover, relative to unfortified dried shrimp where protein denaturation was observed at  $40^\circ\text{C}$  (Schubring, 2009), superior thermal stability was displayed by both VDFS-1 and VDFS-2.

## Conclusion

In the present work, the shrimp was enriched for improvements of its nutritional attributes and energy content by fortification with two fishes (*Catla catla* and *Chela cachius*) along with the addition of corn and rice flours (with or without adding dried ginger). Though VDFS-2 possessed higher shelf-life, antimicrobial activity, carbohydrate and energy content than VDFS-1, VDFS-1 was superior in terms of alkalinity, lower drying time, rehydration ratio and thermal stability than VDFS-2. VDFS-1 exhibited better quality due to remarkable increments in protein,  $\omega$ -3 fatty acids, carbohydrate, ash and other essential elements as compared to raw shrimp. Moreover, VDFS-1 possessed acceptable  $a_w$ , TVBN and histamine content, making it an attractive foodstuff. Thus, enrichment of shrimp by fortification with low-cost fishes and flours was demonstrated to be an effective protocol. Additionally, the energy-efficient fast vacuum-drying could emerge as a proficient preservation method.

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