

Characterization of quality degradation during chilled shrimp (*Litopenaeus vannamei*) supply chain

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Abstract

Loss of quality in white shrimps (*Litopenaeus vannamei*) during a cold supply chain (0-8°C for 96 hours) was measured and modeled at constant and variable temperature conditions. Quality parameters such as color, Texture Profile Analysis (TPA), Total Viable Count (TVC), Total Non-Volatile Basic Nitrogen (TVB-N), and Sensory Index (SI) were selected as indices of quality. A bulk mean temperature (T_{bm}) function was calculated to describe the effect of storage time and temperature, to which the shrimp were subjected, on the quality indices using stepwise multiple linear regressions ($R^2 = 0.88-0.99$, $SEE = 0.045-15.63$). Color degradation (L^* , a^* , b^* index), SI, and TVC (CFU/g) in cold chain were adequately described by a zero order reaction with R^2 values > 0.9 . In order to reduce the number of variables obtained in TPA, hardness (H), springiness (S), gumminess (G), cohesiveness (Co) and chewiness (Ch), were subjected to multiple linear regression. The hardness, H, turned out to be the most significant parameter ($P < 0.05$). Using the Arrhenius equation kinetic parameters, reaction rates (k , min^{-1}) and activation energy (E_a , KJ. Mole⁻¹.°K) were calculated for all the textural properties. The developed models were used to estimate remaining shelf life in terms of H, TVC, TVB-N and SI at 4 different distribution stages of a supply chain. The predicted values showed a good relationship ($R^2 \geq 0.9$) with the experimental data for all the quality parameters. The correlation matrix of the dependent variables showed that color parameters (L^* , b^*), pH, and sensory index were positively correlated ($P < 0.05$) with H, TVC, and TVB-N, respectively. However, after 84 hours of storage in variable temperature conditions, the level of TVB-N was still within the acceptable range (≤ 25 mg/100 gm N), but samples were unacceptable due to high microbial growth (> 7.5).

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Introduction

Variability in temperature during storage and handling determines quality loss rates and the final level of quality of perishable foods. Seafood, such as shrimp, is highly susceptible to postharvest spoilage, and therefore, handled at low temperatures. Unlike the frozen shrimp market, which mainly serves premium local and export markets, a cold supply chain serves domestic markets. Although, the shrimps are caught and transported alive (submerged in iced water $< 5^\circ\text{C}$), death occurs during transportation from farm to retailers, inducing postmortem changes in quality parameters. Shrimps are put on display for 12-48 hours and then, optionally, spend another 24-48 hours in household refrigerators before consumption.

Various chemical and physical changes take place after harvesting and during storage. From a consumer point of view, color fading (Chandrasekaran, 1994), and odor and textural changes (Tsironi *et al.*, 2009) are the most important quality parameters. These

quality losses are due to complex physico-chemical reactions such as lipid oxidation, de-naturation of protein, sublimation, and re-crystallization of ice. A detailed account of chemical changes (lipid oxidation, volatile basic nitrogen) in frozen shrimp quality has been reported by Riaz *et al.* (1990). Tsironi *et al.* (2009) modeled shelf life of frozen shrimp in variable temperature conditions. They included color, texture, pH, microbial quality, and T-VBN as the indices of quality. The rate of quality deterioration in time and temperature domain was expressed by the Arrhenius equation ($E_a = 118$ to 156 kJ/mol). Yamagata and Low (1995) measured quality loss in terms of formaldehyde changes in iced shrimp and recommended 4 days of shelf-life. However, complex biochemical changes cannot be easily related with consumer's perception of quality (Sloof *et al.*, 1996). Nevertheless, both physical and chemical quality indicators have been used to quantify shrimp freshness. Zeng *et al.* (2005) compared cold water shrimp (*Pandalus borealis*) stored under chilled (1.5°C) and super chilled (-1.5°C)

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conditions (6 days of storage) in terms of microbial growth, TVC, pH, and TVB-N.

Quality parameters

Color is a parameter of foremost importance, measured in terms of Hunter color parameters (L^* , a^* , and b^*), and the total change in color (ΔE) (Ahmed and Shivhare, 2001). Translucent appearance of fresh shrimp turns darker with time, which is quantified in terms of the b^* -value (yellowness) and L^* -value (lightness), during shrimp storage. Color is measured at the time of harvest, prior to cooking, and after cooking to determine the change. The change in color is dependent on sample composition and storage temperature. A zero order relationship has been used to describe the change in b -value over a period of time (Tsironi *et al.*, 2009).

Texture has been attributed as one of the most important quality factor for a product's acceptability (Monaco *et al.*, 2007) and is defined as an expression of structural, mechanical and surface attributes detected through human senses (Szczesniak, 2002). Texture depends on a sample's physico-chemical properties and human perception. Various eating preferences have been identified in developing textural profile analysis of solid foods. Among them, hardness, cohesiveness, and springiness are the most relevant to sea foods. Hardness is estimated during the first mastication, i.e., force is applied on the food product, resulting in a linear curve until the first peak, which represents a sample's strength. Other parameters derived from the curve are described by Bourn (1978).

pH is an indication of acidity, which is also related with the growth of microbes in the samples. The activity of microorganisms is the prime cause of spoilage in fresh seafood since they give rise to undesirable flavors and odors. Total Viable Count (TVC) is used as the acceptability index in standards, guidelines and specifications (Qingzhu *et al.*, 2003). Total Volatile Basic Nitrogen (TVB-N) is an indicator of seafood freshness primarily due to spoilage bacteria (Huss, 1995). However, this quality indicator cannot be attributed to solely microbial spoilage due to the fact that other contributing factors, such as autolytic enzyme reactions do exist.

Sensory evaluation is conducted to complement chemical and physical methods. This determines the degree of reliance on objective (instrumental) methods. A sensory index has been developed for fresh shrimps, based on appearance, feel (texture), and color (luster) of shrimp used by buyers and inspectors in the market (Sveinsdottir *et al.*, 2003).

Zeng *et al.* (2005) has divided sensory quality characteristics into 5 classes ranging from excellent to spoiled. Inter-relationships with sensory and instrumental tests have been reported for cooked shrimp texture, color, and general appearance (Giménez *et al.*, 2012).

Although, a number of papers have been published on modeling shelf life quality in frozen shrimp (Nielsen and Jorqensen, 2004; Tsironi *et al.*, 2009), modeling loss of quality in chilled shrimp from the perspective of supply chain management has not been given due attention due to the fact that fresh shrimps are mostly traded in conventional wet markets where modern quality assurance requirements are not in place. However, there is an increasing demand for monitoring, controlling, and recording critical parameters throughout a product's life cycle, i.e., from production to consumption. Among other factors, temperature during handling and storage is the most important factor that directly determines shelf life of a product. In actual practice, temperature during handling and storage vary from the recommended temperature range in a cold distribution chain (Giannakourou *et al.*, 2006). With modern temperature measuring and recording devices such as RFID (Radio Frequency Identification) temperature sensors (Jedermann *et al.*, 2009), cellular and Zig-Bee based sensors (Ruiz-Garcia *et al.*, 2008), it is now possible to wirelessly measure and record temperature in almost all the stages of supply chain as an integrated traceability system (Ruiz-Garcia and Lunadei, 2010). The data generated through a monitoring system can be used to develop empirical quality models and to establish temperature dependency of most of the quality deteriorating reactions. In addition, empirical models are needed for developing quality assignment models representing a homogeneous group of consumers for their quality perception (Sloof *et al.*, 1996). To make use of the collected data of time and temperature, quantitative relationships between storage conditions and shelf life are relevant to the current market need (Giannakourou *et al.*, 2006). Information of shrimp quality loss patterns will help in developing inventory replenishment models based on actual quality (Taoukis, 1999).

Therefore, the objective of this study was to characterize the quality deterioration behavior of shrimp (*Litopenaeus vannamei*) stored and handled at low temperatures (0-8°C), specifically, to study the changes in physical, chemical, and microbial indices of spoilage at constant and variable storage temperatures.

Materials and Methods

Live white shrimp (*Litopenaeus vannamei*) were captured from a local fresh water farm located in Pathum Thani province (Thailand) during March 2012. Samples were transported to a laboratory in iced box, washed thoroughly with fresh water and chlorine, and sorted to have equal size, and stored.

Two different storage scenarios were used: (i) fixed storage temperatures, i.e., 0, 3, 5, and 8°C for monitoring changes in quality and, (ii) a single lot undergoing fluctuating storage temperature in the range of 0–8°C to mimic the actual commercial handling. For the first scenario, separate commercial refrigerators (SANYO SR-F415) were used and for the latter, specially designed cooling chambers were used to store shrimps (Figure 1). The cooling chamber was consisted of 3 identical containers to collect data in triplicate. Each container was coiled with duct containing cooling media (Freon) through a compressor. A K-type thermocouple was used, to insert in 3 different positions in the container, to record temperature output per second with the help of a digital temperature controller and a data logger. The time-temperature controller was programmed to resemble the real supply chain temperature scenario. After placing the samples inside the chamber, air from inside the chamber was pumped out using vacuum pump to avoid initial quality loss due to the presence of oxygen. The temperature was varied between 0–8°C over a period of 4 days (Figure 2). There was no fluctuation. The resolution of measuring equipment was 0.1°C. According to manufacturer's specification there was an accuracy tolerance of 0.01%+0.03°C of reading (Center 309 Temperature controller and Data Logger, Center Technology Group, Taipei, Taiwan). The samples were collected every 12 hours for the quality analysis.

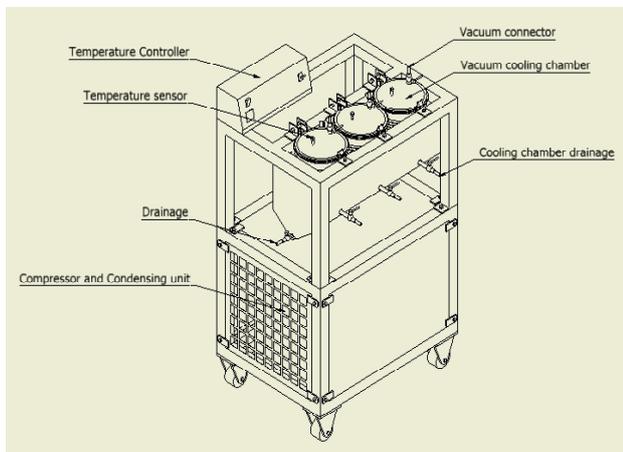


Figure 1. A schematic diagram of cooling chambers to simulate temperature fluctuation in a cold supply chain

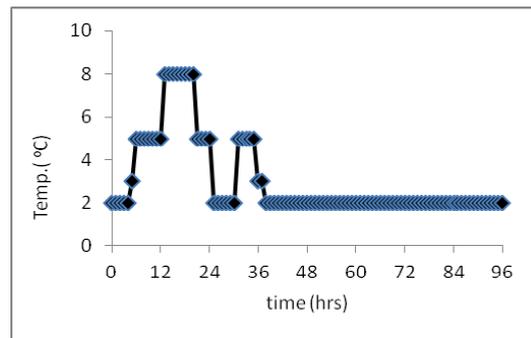


Figure 2. Typical temperature profile of fresh shrimp from harvesting, to retail and household storage.

Determination of quality parameters

Color measurement

Change in color was measured as CIELab values (L^* -value: lightness, a^* -value: redness and greenness, b^* -value: yellowness and blueness), by a Hunter Color meter. The instrument was standardized according to the CIE (Commission International de l'Éclairage) with a standard white reference plate (calibrated as L^* 93.33, a^* -0.91, b^* 1.46). Color measurements were conducted at the end of every storage period at two points of peeled single shrimp samples. The average L^* , a^* and b^* values were converted into total change in color (ΔE), according to the following formulae (Eq. 1):

$$\Delta E = \sqrt{(L_t - L_0)^2 + (a_t - a_0)^2 + (b_t - b_0)^2} \quad \text{Eq 1}$$

where L_0 , a_0 , and b_0 are the initial color values when storage time was zero. The corresponding L_t , a_t , and b_t shows the color values at a given storage period (in hours).

Texture measurement

Change in texture was measured using a standard compression test to a peeled, squared cut and cooked shrimp with a texture analyzer (TA-XT Stable Micro Systems, UK). A flat ended cylinder of 20 mm diameter was selected to mimic a human finger for compressing the samples. The samples were compressed to 30% of height of original sample height. The fleshy part of shrimp was cut into a square with dimensions of 8x8 mm² in order to maintain uniformity in size (Sigurgisladottir *et al.*, 1999; Thybo *et al.*, 1999). The average height of samples was 10 mm.

In order to construct the texture profile, the Texture Analysis (TA) software was programmed to apply double compression. The flat-ended cylinder (P35) approached the sample at the speed of 0.5 mm/s and penetrated 2 mm into the shrimp flesh with a holding time of 5 seconds. Then a second compression was made on the sample, force-

deformation curves were analyzed to calculate texture parameters (Sigurgisladottir *et al.*, 1999; Thybo *et al.*, 1999). Two basic textural parameters such as hardness (g) – maximum force of the first peak – and elasticity (s) were obtained. Other parameters of interest, such as cohesiveness (g.s), gumminess, and chewiness, were derived from the force vs. time plot. Using texture expert system software (developed by Stable micro systems Inc. UK) a double compression was performed on the same sample with a 1 second delay in between for comparison and calculation of parameters.

pH measurement

Samples were prepared by adding 20 ml of distilled water into 5 gm finely minced shrimp meat. The mixture was then homogenized by the help of mechanical homogenizer. pH of a representative homogenized sample was measured by a pH meter (EcoScan pH 5, EUTECH Instrument), which had been calibrated with standard pH buffers of 4 and 7 (AOAC, 1990).

Microbiological analysis

Conventional plate count method suggested by Maturin *et al.* (1998) was used to obtain total plate count from shrimp. Twenty-five grams of shrimp was mixed with 225 ml of sterile phosphate buffer solution (PBS) in a Stomacher bag and blended for 1 min. Three dilutions (10^{-1} , 10^{-2} , 10^{-3}) were prepared and 1 ml of each dilutions was inoculated in a sterile Petri dish. The solidified agar the Petri dishes were inverted and incubated for 48 ± 2 h at 35°C . Total viable counts were determined in terms of colony forming units (CFU) between 25-250, using a colony counter equipped with a magnifying glass.

TVB-N measurement

According to Lucke and Geidel's micro distillation method (Pearson, 1973), TVB-N measurements were made. The method includes steam distillation with MgO using the distillation apparatus. The principle of the method is that total volatile nitrogen is released by boiling flesh directly with MgO, which is then absorbed in boric acid. Amount of released volatile nitrogen is calculated by titrating with sulphuric acid. A shrimp sample weighing 5 g was macerated with 50 ml distilled water. MgO (about 1-2 g) was added, mixed well and then it was transferred into the distilling tube of a Tecator Distillation Apparatus (Model Kjeltec 1026). The distillation was carried out for 3 minutes and the distillate was titrated against 0.1N sulphuric acid.

TVB-N was calculated in two replicates for each sample.

The value of TVB-N was calculated by Eq. 2 (Botta, 1995):

$$TVB - N \left(\frac{\text{mgN}}{100\text{g flesh}} \right) = \frac{\text{Normality of acid} \times 1.4 \times 100}{\text{sample mass in g}} \quad \text{Eq 2}$$

Sensory analysis

Trained panelists were requested to evaluate samples of cooked shrimp on a 3-point scoring scale (where 3 and 1 represented highest and least quality, respectively) for descriptive sensory parameters such as likeness vs. dislikeness of odor, appearance, and texture; SI was determined by Eq. 3 (Huss, 1995; Kreyenschmidt, 2003):

$$\text{Sensory Index} = \frac{2C + 2O + 1T}{5} \quad \text{Eq 3}$$

Where C = color, O = odour, T = texture.

Sensorial score was described against time by linear regression. Samples were considered "spoiled" when the SI reached 1.8 (Kreyenschmidt, 2003).

Data analysis

One way Analysis of Variance (ANOVA) was used to study the effect of storage temperature over time. Multiple linear regressions were used to measure response of time and temperature combination as independent variables against dependent variables of quality loss factors.

Temperature dependence of the quality loss rate is mathematically represented by the Arrhenius equation: Changes in intrinsic quality parameters (response variable y) were modeled with first order kinetic equation (Eq. 4).

$$y = e^{-kt} \quad \text{Eq 4}$$

The initial conditions: $y=1$ at $t=0$ where k is rate of reaction, a constant (min^{-1}), and largely depends on temperature, therefore, a relationship with temperature is given by Eq. 5:

$$k = k_0 \exp\left(\frac{E_a}{RT}\right) \quad \text{Eq 5}$$

Where k_0 is constant pre-exponential factor dependent on a range of temperature in reactions, E_a is the flow activation energy (KJ/mol $^{\circ}\text{K}$), R is universal gas constant (8.314 kJ/mol. $^{\circ}\text{K}$), and T is absolute temperature ($^{\circ}\text{K}$).

Table 1. Total Change in Color at the end of storage period (84 hours)

Temp. °C	0	3	5	8
L-L ₀	-4.65±0.11 ^a	-5.34±0.13 ^a	-7.03±0.04 ^b	-7.9±0.12 ^b
a-a ₀	1.58±0.1 ^a	1.52±0.04 ^a	1.63±0.01 ^a	2.12±0.07 ^{ab}
b-b ₀	-26.39±0.01 ^a	-25.58±0.2 ^a	1.63±0.01 ^b	1.25±0.01 ^b
ΔE	5.78±0.073 ^a	6.38±0.13 ^{ab}	8.01±0.02 ^{bc}	10.06±0.2 ^d

^aSignificantly different groups at P<0.05 are shown in superscript letters
^{**}Calculated using Eq. 1.
^{***}Measured in triplicate, ± = standard deviation.

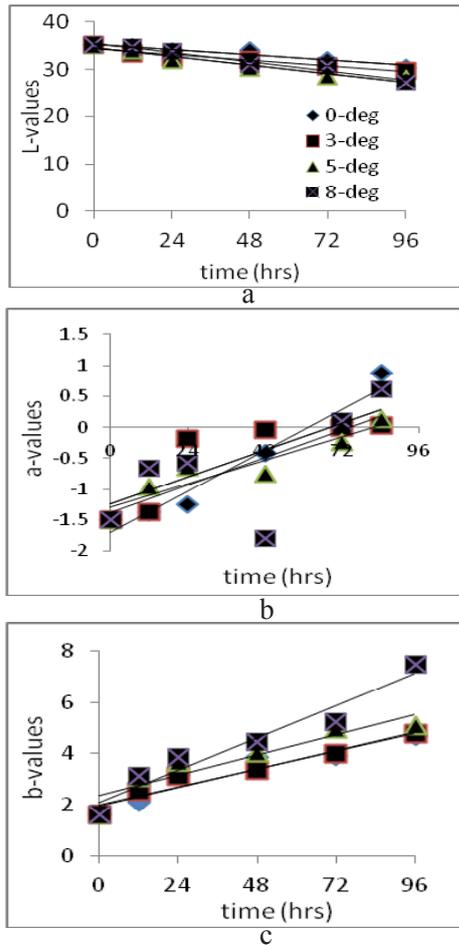


Figure 3. Effect of storage temperature on color of shrimp stored at 0-8°C: (a) Lightness (b) redness (c) yellowness

Results and Discussion

Effect of fixed storage temperature on quality parameters

Color degradation

The initial shining color of shrimps starts to look dull as soon as their death occurs. However, samples did not show much yellowness in the first 12 hours of storage at all temperatures. At temperatures 5 and 8°C, the samples appeared darker and blackening occurred near the upper region of a shrimp. Hard shell was removed before taking measurements. The

Table 2. Parameters of zero order regression of shrimp color at 0-8°C storage temperature

Parameters	a-value	b-value	L-value
0°C			
Slope	0.0253	0.03	-0.047
Intercept	-1.66	1.98	35.2
R ²	0.98	0.9	0.93
3°C			
Slope	0.016	0.032	-0.075
Intercept	-1.179	1.73	34.4
R ²	0.71	0.99	0.95
5°C			
Slope	0.0145	0.042	-0.076
Intercept	-1.27	1.98	34.4
R ²	0.89	0.98	0.95
8°C			
Slope	0.0174	0.068	-0.08
Intercept	-1.36	1.99	35.4
R ²	0.5	0.98	0.95

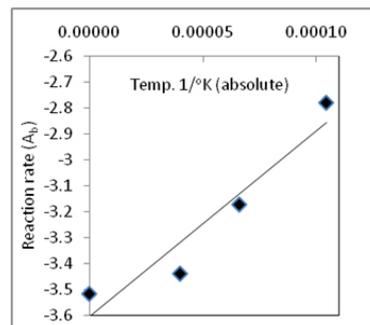


Figure 4. Relationship between color loss reaction rate and storage temperature (1/°K absolute)

color of underneath flesh changed from translucent white to yellowish-orange and finally to a dark color over time.

Table 1 shows total change in color in terms of difference between final value and initial obtained from a color meter during the entire storage period. It can be seen that a temperature difference of 2-3°C had a significant effect on change in color; for example, b-value was significantly different at 3 and 5°C, whereas total change in color was significantly different at all storage temperatures.

Changes in L, a, b values of shrimp during storage could be conveniently modeled by a zero order equation (Eqs. 6-8):

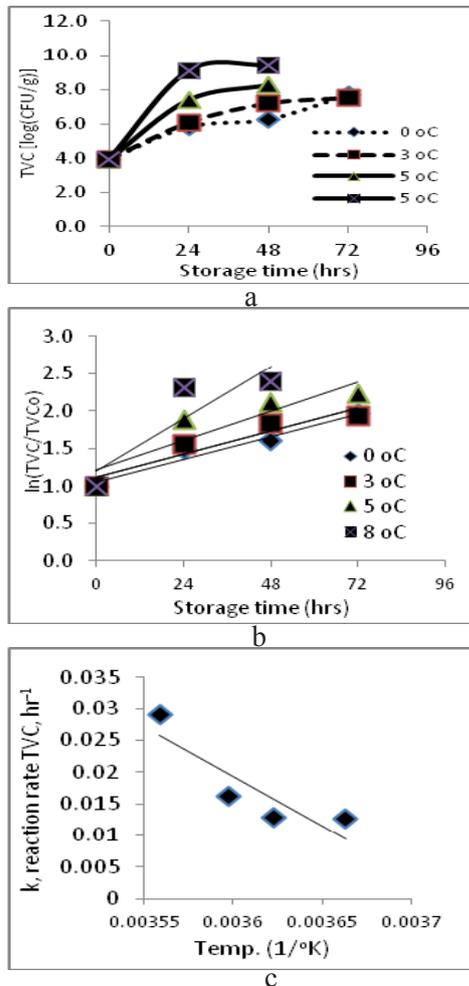
$$\begin{aligned}
 L^* &= A_L \cdot t + L_0 \\
 a^* &= A_a \cdot t + a_0 \\
 b^* &= A_b \cdot t - b_0
 \end{aligned}
 \quad \text{Eq 6-8}$$

where A_L, A_a, A_b are rate constants of the reaction, and t is the storage time (hrs). The parameters are summarized in Table 2 and Figures 3 (a, b and c).

Shrimp samples darkened with temperature and time; the lightness value at the end of storage period relative to the lightness at the day of harvest reduce linearly (P < 0.05) with time at each storage temperature (Figure 3a). The a-values (redness) increased over time and temperature without any visual appearance of red, which is an indication of cooking. The b values increased sharply over time

Table 3. Kinetic parameters of changes in textural quality of shrimps stored at 0-8°C

Texture attribute	E_a (KJ.Mole ⁻¹ .°K)	Reaction constant, k_0	Expression	R^2
Hardness (g)	-10.03	-0.0361	$\ln(H/H_0)=[46.93(1/T_{abs})-0.211]*t$	0.975
Elasticity (s)	-10.02	-0.0342	$\ln(E/E_0)=[405.53(1/T_{abs})-1.517]*t$	0.932
Cohesiveness (g.sec.)	-14.96	-0.0082	$\ln(C/C_0)=[23.634(1/T_{abs})-0.0946]*t$	0.899
Gumminess	-31.15	-0.0184	$\ln(G/G_0)=[105.89(1/T_{abs})-0.405]*t$	0.961
Chewiness	-14.57	-0.0329	$\ln(Ch/Ch_0)=[119.79(1/T_{abs})-0.472]*t$	0.902

Figure 5. (a) Effect of storage temperature on Total Viable Count (TVC), (b) linear representation of normalized TVC (c) effect of temperature on the reaction rate, k .

at all temperatures, and fitted very well into a zero-order kinetic model. In all cases, a high correlation coefficient (R^2), ranging between 0.71 and 0.99, was obtained. However, at higher storage temperature of 8°C, a poor correlation was obtained due to onset of spoilage after 36 hours. Despite a significant variation in color in terms of Hunter parameters, a clear shift from yellow to red hues was not evident at a lower temperature range.

In order to determine temperature dependency of the reaction rate of yellowness, the A_b values obtained during linear regression (Figure 4) were plotted against absolute temperature (°K, $1/T+273$). The resulting equation ($A_b = 7203.7(1/T_{abs}) - 3.6063$,

$R^2 = 0.9105$) was inserted in Eq. 9.

$$b^* \text{-value} = [7203.7(1/T_{abs}) - 3.6063] \times t - 1.98$$

where the intercept (1.98) was fixed to initial b^* -value at the start of storage period. The activation energy (E_a) of the reaction was calculated as 60 (KJ. Mole⁻¹.°K) for a temperature range of 0-8°C, which signifies shrimp sensitivity to temperature. For quality monitoring purpose, b values can sufficiently be used to determine level of quality.

Changes in textural quality

The initial values of texture attributes hardness (g), springiness (elasticity), cohesiveness (g.s), gumminess, and chewiness at zero storage time were: 115.02 ± 1.5 , 1.8 ± 0.034 , 0.95 ± 0.01 , 1.3 ± 0.026 , 149.87 ± 2.5 , and 142.38 ± 1.67 , respectively. For simplicity, data obtained from texture analyzer of each attribute was normalized by dividing with the initial value and then plotted against storage time in a semi-log fashion to remove non-linearity, and then fitted with a first order equation yielding $R^2 > 0.9$ (Table 3).

Hardness and elasticity were observed decreasing significantly after 12 hours of storage. The samples appeared soft and mushy after 48 hours of storage at higher temperatures (5-8°C). Other attributes also showed the effect of deterioration, however, the rate of change was less than the hardness and elasticity, as indicated by the negative activation energy and the rates of reaction. Monaco *et al.* (2007) also reported high accuracy of prediction in the cases of hardness and springiness, as compared to the other TPA parameters. Although cohesiveness, gumminess, and chewiness are good indices for characterizing sensorial properties, their representation in accurate prediction was inadequate. Therefore, only hardness and elasticity were sufficient to model deterioration.

Changes in pH and microbial growth pattern

Initial pH of samples was 6.62, which steadily increased to 7.6. The results were in accordance with the published data (Riaz and Qadri, 1990) and also confirmed by the microbial growth, due to which bio-chemical changes took place. Bacterial contamination was estimated in terms of total viable cells: mesophilic and psychrophilic cell counts.

In general, TVC increased continuously throughout the storage period of 84 hours ($P < 0.05$) at all temperatures. The initial microbial load, in terms of viable cells, was 3.9×10^5 log (CFU/gm), which increased depending on the temperature (Figure 5). The initial load was higher, but within the acceptable industrial standard [$< 1 \times 10^6$ log (CFU/gm)] and

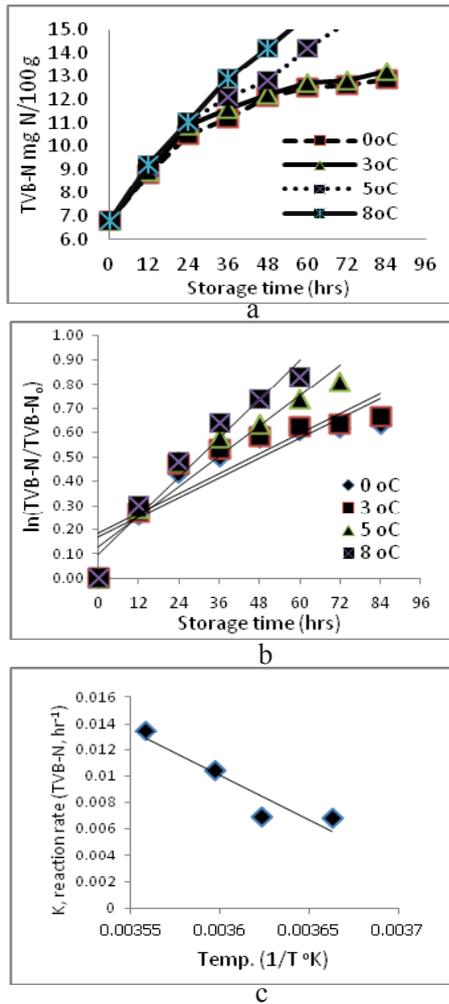


Figure 6. (a) Effect of storage temperature on total volatile basic nitrogen content in fresh shrimps (b) linear representation of normalized TVB-N (c) effect of temperature on the reaction rate, *k*.

values reported in the literature (Zeng, 2005). The samples were considered spoiled when total bacterial count reached 7.5×10^8 CFU/g. TVC was modeled (eq. 10) as shown in Fig. 5, yielding a high correlation coefficient ($R^2 > 0.9$):

$$TVC = e^{-(155.8(1/T)+0.5802)t} \quad \text{Eq 10}$$

($R^2 = 0.9-0.95$)

Where:

TVC = total bacterial count [log(CFU/g)]
 t = time (hours)

Changes in total volatile basic nitrogen

It was obvious that TVB-N increased as the storage time increased at all the storage temperatures. At higher temperatures the change was steady, whereas at 0 and 3°C, the level of TVB-N tended to stabilize after initial increase. There was a significant difference in TVB-N levels after 24 hours of storage at all temperatures ($P < 0.05$). In some studies it has

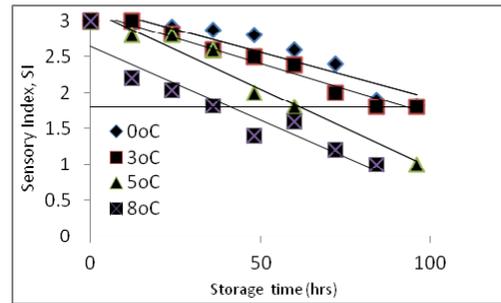


Figure 7. Change in Sensory Index during storage

been reported that TVB-N decreased after an initial period of 4 days of storage (Ozogul *et al.*, 2011). The possible explanation of such phenomena can be related to the experiments that have been conducted in iced storage, in which melting of ice washed away TVB-N, which results in decreased levels. In the current study, storage temperatures were maintained in a dry chamber; therefore, a decrease of TVB-N levels was not observed.

It is recommended to use TVB-N if sensory evaluation indicates doubt about freshness. Depending on shrimp culture conditions and harvesting practices, a critical limit of 25-35 mg-TV B-N/100 g has been established (Einarsson, 2001).

A relatively poor correlation between storage time and TVB-N was observed at low temperatures (0-3°C, $R^2 = 0.7$), whereas the correlation improved at higher temperatures (5-8°C, $R^2 = 0.9-0.94$) when a linear curve was fitted (Fig. 6). The relationship between TVB-N, time and temperature of storage can be explained in exponential form (Eq. 11):

$$TVB - N = e^{(-67.279(\frac{1}{T_{abs}})+0.2523)t} \quad \text{Eq 11}$$

($R^2 = 0.9-0.94$)

Where:

TVB-N = total volatile basic nitrogen, mg N/100 g
 T_{abs} = temperature (absolute), °K
 t = time, days

Sensory evaluation

The sensory index (SI) decreased linearly with time at all storage temperatures. The samples were considered spoiled when SI reached 1.8 and below (Kreyenschmidt, 2003). As estimated, at higher storage temperatures, the spoilage point was reached faster than at the lower temperature. At 0°C, the samples were still in acceptable condition by the panelists by the end of the storage period. At higher temperatures and longer storage time, fruity, rotten, sulphhydryl odors due to number of volatile aldehydes, ketones, esters, and sulphides produced by *Pseudomonas* spp. in iced seafood was noticed (Huss, 1995).

Table 4. Correlation between intrinsic quality parameters of shrimp stored at 0°C and sensory index

	L	a	b	Hardness, N	pH	TVC	TVB-N
a value	-0.955						
b value	-0.881	0.915					
Hardness, N	0.804	-0.827	-0.918				
pH	-0.769	0.745	0.829	-0.948			
TVC	-0.958	0.899	0.989	-0.972	0.992		
TVB-N	-0.787	0.774	0.913	-0.959	0.888	0.914	
Sensory Index	0.975	-0.959	-0.871	0.779	-0.828	-0.944	-0.635

(P < 0.05)

Table 5. Results of step-wise multiple linear regression to estimate quality parameters of shrimps stored at variable storage conditions

Temp.	Predictors	a ₀	a ₁	a ₂	a ₃	R ²	SEE	F*
Hardness (N)	t	92.265	-1.154			0.896	12.48	51.667
	T _{bm}	120.442	-1.347	-6.972		0.965	7.96	68.313
	T _{bm} , t ²	127.877	-2.134	-6.431	.010	0.91	0.94	3.33E3
TBC	t	106.045	-1.380			0.887	15.63	47.140
	T _{bm}	124.758	-2.940	.019		0.980	7.28	119.729
	T _{bm} , t ²	139.755	-2.980	.018	-3.912	0.994	4.28	234.564
TVB-N	t	104.708	-1.390			0.881	14.89	52.656
	t ²	121.085	-2.75	.016		0.956	9.08	76.439
	t ² , T _{bm}	133.502	-2.87	.016	-0.648	0.997	2.27	836.703
Sensory Index	t ²	3.04	-0.982			0.95	0.045	136.56

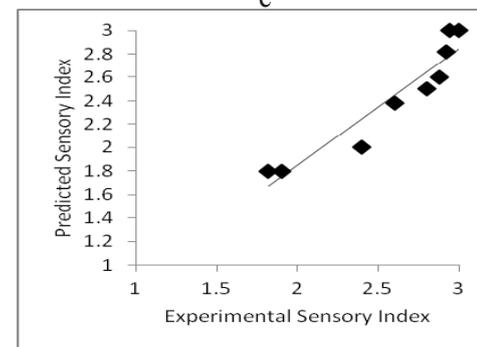
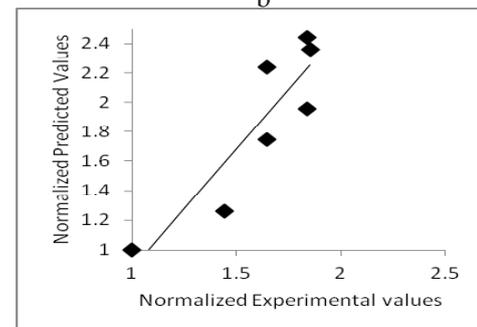
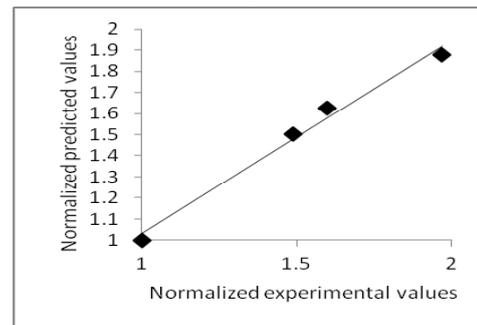
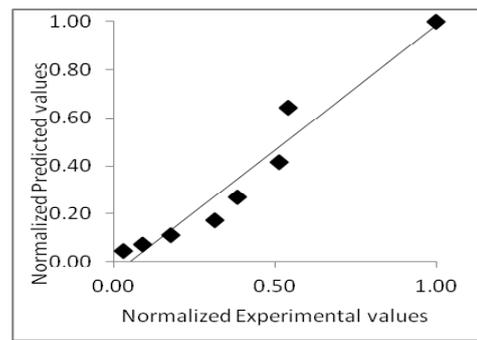
T_{bm} = bulk mean temperature
 *Significant P < 0.05

The correlation (R²) between all storage temperatures and SI was between 0.85-0.9, which signifies that shelf life can be evaluated through subjective assessment using a 3-point sensory index (Fig. 7). The panelists were able to differentiate effect of constant storage temperatures on sensorial properties (P < 0.05) such as color, odour, and texture.

Inter-relationship between intrinsic quality parameters

A high correlation of 0.99 between TVC and pH was observed. Similarly, SI had a high and significant correlation between color values (L*, a* & b*) and TVC. Low but significant correlation was observed with TVB-N and hardness.

A correlation matrix showed good relationship with high magnitude for most of the parameters (Table 4), confirming their significance to be used for shelf life prediction. It was also concluded that SI scores were in agreement with the instrumental methods.



	Slope	R ²
Hardness	1.0384	0.942
TBC	0.916	0.986
TVB-N	1.752	0.762
SI	0.892	0.996

Figure 8. Cross validation of developed models for (A) Hardness (N) (B) Total Viable Count [log (CFU/gm) (C) TVB-N mg/100 g (D) Sensory Index

Effect of variable storage temperature on quality parameters

In order to evaluate a collective effect of

Table 6. Determination of remaining shelf life and quality level at each distribution stage

Parameter	Loss in Quality Level at Different Distribution Stages*				Threshold quality level**
	First Stage ($T_{eff}=2^{\circ}C$)	2 nd Stage ($T_{eff}=6.5^{\circ}C$)	Third Stage ($T_{eff}=3.5^{\circ}C$)	Fourth Stage ($T_{eff}=2^{\circ}C$)	
Hardness (N)	115	62	59	45	≤ 20
TVC log(CFU/gm)	3.9	5.8	6.2	7.7	≤ 7.5
TVB-N(mg/100 gm)	6.8	9.8	11.2	12.5	≤ 5
Sensory Index	3.0	2.94	2.92	2.8	≥ 1.8
Remaining Shelf life (hrs)	84	72	60	12	

*quality level at corresponding effective storage temperature (T_{eff} °C), **as reported for TVB-N (Einarsson, 2001), TBC (Maturin, 1998), & Sensory Index (Huss, 1995) respectively. For hardness, the corresponding S.I. level was used.

different time and temperature scenarios, the bulk mean temperature (T_{bm}) function, as shown in Eq. 12 was used.

$$T_{bm} = \frac{\int T \cdot dt}{dt} \quad \text{Eq 12}$$

T_{bm} is a constant temperature which induced a change in the product properties equivalent to the fluctuating temperature history during the same storage period (Solomon and Jindal, 2007) described by the sum of all time-temperature combinations averaged over entire storage period. The changes in quality parameters during storage under the fluctuating temperature conditions can be described by using stepwise multiple regressions in which the dependent variables were the normalized values (ratio of values at time t to initial value) of the quality parameter. The functional form of important parameters is as follows:

Quality Parameter	Measured as	Functional Form
Texture measurement	Hardness (N)	$\frac{H_t}{H_0} = f(T_{bm}, t)$
Total Viable Count	Log (CFU/gm)	$\frac{TVC_t}{TVC_0} = f(T_{bm}, t)$
Total Volatile Basic Nitrogen	TVB-N mg N/100g	$\frac{TVBN_t}{TVBN_0} = f(T_{bm}, t)$
Sensory Index	On a scale of 1-3	$\frac{SI_t}{SI_0} = f(T_{bm}, t)$

F-test significance determined which term to be included on the right hand side of the above equations. Table 5 shows predictors and corresponding coefficients of each equation. Four parameters of interest such as hardness, TVC, TVB-N, and SI were selected to measure their response to these time-temperature combinations. All combinations of predictors were significant at $P < 0.05$ from 0 to 3rd order polynomial arrangement ($R^2 = 0.881-0.99$, $SEE = 0.045-15.63$), except the SI for which only the square of time (t^2) was sufficient to predict sensory scores. This could be explained by the fact that human receptors cannot perceive the change in sensory quality accurately, which resulted in less

variability in data, hence, yielding an equation with fewer terms.

Cross validation of developed models

By using another set of data that was not used for developing models, cross validation was performed. The values obtained from developed models were plotted against experimental values. The models were evaluated based on linear fit of data in terms of correlation coefficient (R^2) and the slope of the fitted line (Figure 8).

According to temperature profile depicted in Figure 2, four distinctive distribution stages were identified. By inserting average temperature at each stage with the models shown in Table 5, a quality level at each stage was determined. This allowed the estimation of remaining shelf life by using a pre-determined threshold level of quality. As it can be seen in Table 6, hardness and TVB-N did not reach the limit during 84 hours of storage, however, samples were unacceptable due to microbial growth.

Conclusion

The developed relationships between time-temperature history and quality parameters characterize the spoilage behavior of shrimps distributed through a cold chain and can be employed for predicting remaining shelf life of shrimps if time-temperature data is monitored and recorded at all stages of a supply chain. It was observed that a narrow temperature fluctuation of 2-3°C can significantly reduce the keeping quality and affect freshness. Therefore, measurement of the intrinsic quality indices by instrumental methods and human judgment, correlated with time-temperature history, is important to determine the quality level and remaining shelf life. Moreover, the developed kinetic models for representing the physical quality indices, such as textural and color properties in iso-thermal conditions with the kinetic parameters (reaction rate, activation energy), are useful for the development of stock replenishment schemes during distribution. Also, as in this study, a significant positive correlation was found between physical and chemical quality indicators, suggesting that simple measurement of pH and color parameters (L^*, b^*) can be used to predict TVC, TVB-N and hardness of shrimps, which are complex and difficult to assess at distribution centers and retail outlets. The empirical modeling approach, using bulk mean temperature function to account for the quality changes during fluctuating time-temperature regimes, provides an indication of quality level of samples. This information is important for pricing, grading, and shipment prioritization.

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