Kinetics of changes in shelf life parameters during storage of pearl millet based *kheer* mix and development of a shelf life prediction model

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Abstract Pearl millet, dairy whitener and sugar powder were blended for preparing pearl millet *kheer* mix. Pearl millet based *kheer* mix samples were stored at 8, 25, 37 and 45 °C under nitrogen flushing environment. Changes in HMF and TBA formation in the dry mix and sensory changes in reconstituted *kheer* were studied upto 180 days. In fresh dry mix, the average value of HMF recorded was 4.87 µmol/g which increased to 11.23, 13.67, 18.13, and 21.43 µmol/g at 8, 25, 37 and 45 °C, respectively after 180 days of storage. From an initial value of 0.067, the TBA value increased to 0.219, 0.311, 0.432 and 0.613 at 532 nm at 8, 25, 37 and 45 °C, respectively after 180 days of storage. Data generated from the chemical kinetics of HMF and TBA development that progressed during storage of pearl millet *kheer* mix were modeled using Arrhenius equations to predict the shelf life of the product. Changes in HMF and TBA followed first order reaction kinetics. It was found that the potential shelf life of the pearl millet based *kheer* mix was 396 days at 8 and 288 days at 25 °C, respectively.

Keywords Pearl millet based *kheer* · Shelf life prediction modeling · Nitrogen flushing · Hydroxymethyl furfural · Thiobarbituric acid

Introduction

Cereal based desserts, popularly known as *kheer*, *dalia* and *phirni* are produced mainly from the rice or wheat in

different forms viz., whole or broken grains, grain fraction such as semolina and flour. As most of the desserts have a poor shelf life, new processes have been developed to convert them into dry forms in order to have a better shelf life and also for ease of consumption. Several dry mixes have been developed in the past to enhance the shelf life and to provide convenience to consumers (Singh and Shurpalekar 1989; Singh et al. 1990; Jayanthilaken et al. 2000; Jha et al. 2002; Pelembe et al. 2002; Sadana and Chabra 2004; Mridula et al. 2008; Kadam et al. 2011; Bunkar et al. 2012).

Pearl millet (PM) (*Pennisetum typhoides*; Hindi Synonym: *Bajra*) is the sixth most important cereal in the world and is widely cultivated in Asia, Africa and the USA (Abdelrahman and Hosney 1984). It is a good source of energy, fibre, oil and carbohydrates (Singh and Shurpalekar 1989; Narwade et al. 2003; Rai et al. 2008). The popped millet and fiber-regulated millet flakes (Hadimani and Malleshi 1993) are utilized mainly in developing formulations for food supplements or weaning foods (Bhaskaran et al. 1999). PM is also finding increased applications in new food product development including desserts (Jha et al. 2011; Bunkar et al. 2012).

The need for more rapid determination of shelf life has generally become greater. The situation is much more pressing when the shelf life of a product is expected to be long ranging from several months to a few years. The effect of elevating temperature on many chemical reactions as well as adverse changes in food during storage is well known - implication is that at a higher temperature, any adverse effect and hence shelf life may become apparent in a much shorter time (Labuza and Schmidl 1985). Kinetic parameters, such as order of reaction, rate constant and activation energy are important from the point of view of predicting food quality loss (Nisha et al. 2005).

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Kinetics of colour development (from Maillard-type browning reactions) at high temperature were studied in aqueous solutions containing glucose and glycine and it was reported that colour development could be described by first-order reaction kinetics (Ghazala et al. 1991). Free and total hydroxymethylfurfural (HMF) in powdered infant formulae during storage at 55 °C increased in a nitrogen atmosphere. The 90-day storage in a nitrogen atmosphere produced more than eight times the free-HMF than that produced under oxygen (Guerra-Hernandez et al. 2002). The progress of the Maillard reaction in dried infant formula was monitored for 9 months of storage at 20, 30 and 37 °C. HMF content increased at all the temperatures of storage and based on this increase, an equation was derived to predict the shelf-life of such products (Albala-Hurtado et al. 1998). Non-enzymatic browning in cheddar cheese powder during storage in the range of 20–40 °C was found to follow zero-order reaction kinetics with activation energies and Q_{10} values being in the range of 15.1–22.3 kcal/mol and 2.2–3.5, respectively (Kilic et al. 1997). Similarly, in another study, it was reported that change in colour of mango powder during storage follows first-order reaction kinetics (Jaya and Das 2005).

Thiobarbituric acid reactive substances (TBARS) is measure of the formation of secondary oxidation products e.g. carbonyls, being responsible for the sensory impact of lipid oxidation (Hall and Anderson 1985) and this method has been found to correlate well with sensory quality of WMP (Stapelfeldt et al. 1997). Several studies in the past have shown the TBA value to increase with storage temperature and to double after 70 week storage at 30 °C compared to 20 °C irrespective of the heat treatment measured as WPNI (Toohey et al. 1981; Ipsen and Hansen 1988). The oxidative deterioration of instant *kheer* mix powder measured in terms of TBA value followed zero-order reaction kinetics and Arrhenius plot clearly showed temperature dependence of the rate constants. The Arrhenius constant and Q_{10} values were $7.302 \times 10^{10} \text{ Mwk}^{-1}$ and 2.6, respectively (Jha and Patel 2012).

As PM dry *kheer* mix was a new product aimed for ease of reconstitution and longer shelf life, it was considered appropriate to undertake accelerated shelf life testing at 8, 25, 37 and 45 °C for a period of 180 days for studying kinetic changes during storage on the basis of HMF and TBA formation and for developing models for predicting its shelf life under storage conditions. The interrelationship between sensory properties and changes in HMF and TBA were established. The shelf-life prediction model which was developed based on the kinetic constants and the relationship between sensory and chemical parameters could be useful in predicting the shelf life of dried PM *kheer* mix powder. The findings of the present work would help not only in the prediction of the shelf life of dry PM *kheer* mix but would also

be useful for determining the shelf life of several other dried foods, which are specially relevant to tropical countries.

Materials and methods

Materials PM grains (*Pennisetum typhoides*) were obtained from Indian Agricultural Research Institute, New Delhi, India. Powdered sugar and dairy whitener (Everyday brand, Nestle India Pvt. Ltd., Moga, India; protein=17.6 g/100 g, total carbohydrate=50.9 g/100 g, sugar=23 g/100 g and fat=18.1 g/100 g) was used in the formulation of dry PM based *kheer* mix. Cardamom (*elaichi*) powder as a flavoring agent was procured from the local market of Varanasi, India.

Production of PM based dry kheer mix PM grains were dehulled using wooden pestle and mortar with sprinkling of water to loosen its outer coat, followed by winnowing and washing with water thrice. Thereafter, these grains were spread to form a 1 cm thick layer and allowed to sun dry for 1 h and 45 min followed by autoclaving (TOMY SX-500, Japan, High Pressure Steam Sterilization System) at 121 °C for 15 min. Autoclaving was done to soften the PM grains as it was to be a ready-to-reconstitute product. To dry the sterilized/moist product, before incorporating in the dry mix, it was held at 35 °C for 1 h 45 min. This was followed by dry blending of powdered sugar and dairy whitener with pre-treated pearl millet grains. Cardamom flavour was added @ 0.25 % of the finished product. Procedure for production of PM based dry *kheer* mix was followed as given by Bunkar et al. (2012).

Composition of dry PM kheer mix The moisture content was determined by oven-dry method (AOAC 950.46 1990) and ash content of the pearl millet *kheer* mix was determined by the standard procedure as given in AOAC (1995). Crude protein was determined by Kjeldhal method (IDF 2001) and crude fat was estimated using the automatic SOCS PLUS (SCS 4, Pelican Equipments, Chennai, India) by employing the standard method AOAC (2000).

Packaging and storage of samples Dry PM based *kheer* mix was packaged in polyethylene (PE) laminates (thickness: 350 gauge; size of the pouches: $15 \times 19 \text{ cm}^2$, water vapour transmission rate at 38 °C/90 % RH/24 h: $14\text{--}20 \text{ g.m}^{-2}$, oxygen permeability at 38 °C: $85\text{--}95 \text{ mL.m}^{-2}$) under modified atmospheric conditions (nitrogen flushing in gas mixer Model: MAP Mix 9001 MK, Make: PBI Densensor, Ringsted, Denmark) packaged under vacuum in VAC-STAR* S 220 MP, Make; VAC STAR, Sugiez, Switzerland. Samples were stored at different temperatures viz. 8, 25, 37 and 45 °C for 180 days and withdrawn from storage at regular intervals i.e.

after every 30 days and were analyzed for changes in physico-chemical and sensory attributes.

Analysis of shelf life parameters During storage, the development of HMF was measured according to the method of Keeney and Bassettee (1959) and TBA value was measured using the extraction method of Strange et al. (1977).

Reconstitution of PM based dry kheer mix into kheer Potable water was boiled in a pan and then content of one pouch i.e. approx. 65 g was added to it in the ratio of 1:5 (dry mix: water). This ratio was arrived at after several preliminary trials. Temperature of water was maintained at 90 °C and product was stirred gently for 5 min until desired consistency was obtained. Reconstituted product was allowed to cool to 25 °C before it was subjected to sensory evaluation.

Sensory analysis The freshly reconstituted *kheer* prepared from dry PM *kheer* mix was evaluated for its sensory characteristics such as colour, flavour and overall acceptability (OA) scores based on 9-point Hedonic scale (Amerine et al. 1965) using semi-trained sensory panel consisting of seven

judges drawn from Centre of Food Science and Technology at Banaras Hindu University, Varanasi, India. Sensory evaluation of reconstituted *kheer* samples was done at 25 °C.

Regression analysis Sensory and physico-chemical data were subjected to correlation and regression analysis employing standard statistical methods (O' Mahony 1986). XL STAT 2011 version was used for analysis of variance.

Computation of reaction kinetics The HMF and TBA formation in dry PM *kheer* mix powder was found to obey first order reaction kinetics. The first-order reaction rate constants (*k*) were, therefore, calculated using the following expression:

$$\ln \frac{C}{C_0} = -kt \quad (1)$$

where,

C_0 Initial concentration of the reactant and
 C Concentration of the reactant at time '*t*'

Fig. 1 Change in HMF content and TBA value of pearl millet based *kheer* mix at different temperature under MAP conditions and their Arrhenius plots; **a)** Changes in HMF content Vs storage period (days), **b)** Arrhenius plot of change in HMF content; $1/T, k^{-1}$ Vs $\ln k$, **c)** Absorbance at 532 nm Vs storage period, **d)** Arrhenius plot of change in TBA; $1/T, k^{-1}$ Vs $\ln k$

Arrhenius equation was the most acceptable approach to model a temperature dependent reaction. The temperature dependence of 'k' was described according to the Arrhenius equation:

$$k = A_0 e^{-\frac{E_a}{RT}} \quad (2)$$

where,

A_0 Arrhenius constant
 R Universal gas constant, 8.314 J/mol °K
 T Absolute temperature, °K
 E_a Activation energy, J/mol

The thermodynamic equation parameters were obtained by using the mathematical expressions based on absolute reaction rate theory (Taoukis et al. 1997).

$$k = \frac{k_B \cdot T}{h} e^{\frac{\Delta S^*}{R}} \cdot e^{\frac{-\Delta H^*}{RT}} \quad (3)$$

where,

k_B Boltzmann's constant, 1.38×10^{-23} J/°K
 h Planck's constant, 6.63×10^{-34} J.S
 ΔS^* entropy of activation, J/mol °K
 ΔH^* enthalpy of activation, J/mol

The enthalpy was calculated from activation energy obtained from the experimentally obtained reaction rate constants using the following relationship:

$$\Delta H^* = E_a - RT \quad (4)$$

The free energy of activation (ΔG^* , kJ/mol) was obtained from the following relationship:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

Shelf life prediction modeling The analytical approach for calculating and predicting food quality deterioration involves a set of mathematical relations. This modeling describes the influence of storage time and temperature on the quality parameters of the finished product. For prediction of shelf life, set of mathematical equations were developed combining kinetic functions and the functional relationship of variables relating to physico-chemical parameters and loss of sensory quality. The equations then selected were integrated with the Arrhenius relationship between rate constants and temperature of storage for these variables.

Results and discussion

Proximate composition of the dry PM kheer mix The average moisture, fat, protein, carbohydrate and ash contents of the pearl millet *kheer* mix were 2.8 %, 4.38 %, 5.84 %, 85.88 % and 1.1 %, respectively. In another study, Jha et al. (2011) reported a composition of fat 6.38 %, protein 5.44 %, moisture 34.01 %, total solids 38.23 % and ash 1.23 % for ready-to-eat pearl millet based dairy dessert.

Changes in physico-chemical properties of PM based dry *kheer* mix

HMF

HMF is formed upon heat treatment of milk and milk products by the Maillard reaction, as well as by isomerization and subsequent degradation of sugars (Morales et al. 1998; Baldwin and Auckland 1991). Change in food colour is associated with heat treatment of the food (Seonggyun and Bhowmik 1995). As can be seen from the Fig. 1a, HMF

Table 1 Kinetic parameters related to changes in HMF and TBA formation in pearl millet based *kheer* mix during storage

Variables	Parameters							
	Temperature (°C)	Rate Constant (k), wk ⁻¹	Apparent activation energy (E _a) (kJ/mol)	Frequency factor (Arrhenius constant, A ₀) (M wk ⁻¹)	Q ₁₀	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
HMF	8	2.105×10^{-1}	14.60	2.190×10^6	1.15	12.26	-238.54	67.04
	25	4.059×10^{-1}				12.72	-233.57	69.61
	37	5.070×10^{-1}				13.39	-232.05	71.94
	45	5.097×10^{-1}				14.88	-232.22	73.85
TBA	8	2.319×10^{-1}	28.70	2.912×10^{12}	1.53	26.36	-238.35	67.00
	25	4.698×10^{-1}				26.72	-232.30	69.25
	37	6.516×10^{-1}				27.34	-229.92	71.30
	45	9.874×10^{-1}				27.98	-226.68	72.11

HMF Hydroxy methyl furfural, TBA Thiobarbituric acid

formed as a consequence of progression of maillard reactions increased with the increase in storage time and temperature. In fresh dry mix, the average value of HMF recorded was 4.87 $\mu\text{mol/g}$ which increased to 11.23, 13.67, 18.13, and 21.43 $\mu\text{mol/g}$ at 8, 25, 37 and 45 $^{\circ}\text{C}$, respectively after 180 days of storage of PM *kheer* mix. The formation of HMF was lesser at 8 and 25 $^{\circ}\text{C}$ as compared to 37 and 45 $^{\circ}\text{C}$. This implies that with the increase in storage temperature the formation/development of HMF increases. In SMP, the HMF content increased from 5.68 to 28.43 $\mu\text{mol/g}$ after storage for 240 days at room temperature (Caric et al. 1984). Mrithyunjaya and Bhanumurthi (1987) observed an increase in HMF content from 2.47 to 7.64 $\mu\text{mol/g}$ in dried whole milk on storage at 37 $^{\circ}\text{C}$ for 6 months. Jha and Patel (2012) also reported an increase in HMF content of instant *kheer* mix powder during storage and increase was found to be temperature dependent.

TBA

It is a measure of the formation of secondary oxidation products e.g. carbonyls being responsible for the sensory impact of lipid oxidation (Hall and Anderson 1985) and this method has been found to correlate well with sensory quality of WMP (Stapelfeldt et al. 1997). The increase in TBA values (expressed as absolute OD) during storage of PM *kheer* mix is presented in Fig. 1c. With an initial value of 0.067, the TBA value increased to 0.219, 0.311, 0.432 and 0.613 at 532 nm at 8, 25, 37 and 45 $^{\circ}\text{C}$, respectively after 180 days of storage. To determine the shelf life of PM *kheer* mix, the TBA value of the stored samples were correlated with the storage period for the four temperatures of 8, 25, 37 and 45 $^{\circ}\text{C}$. Several studies have shown the TBA value to increase with storage temperatures and to double after 70 weeks storage at 30 $^{\circ}\text{C}$ compared to 20 $^{\circ}\text{C}$ irrespective of the heat treatment measured as WPNI (Toohy et al. 1981; Ipsen and Hansen 1988). In instant *kheer* mix, the TBA value from initial 0.01 increased to 0.11 after 24 weeks storage at 30 $^{\circ}\text{C}$ while at 37 $^{\circ}\text{C}$, the increase was upto 0.15 after 16 weeks storage (Jha et al. 2002).

Reaction kinetics

The change in HMF content of instant pearl millet based *kheer* mix samples was found to be a first order reaction. The Arrhenius plot ($\ln k$ vs $\frac{1}{T}$) showed a single straight line (Fig. 1b). Polynomial equations were generated to study the change in HMF content at different storage temperatures studied (Table 5). The activation energy,

Table 2 Changes in sensory scores* of reconstituted pearl millet based *kheer* during storage at different temperatures

Storage period (Days)	Colour (Max. 9)				Flavour (Max. 9)				Overall acceptability (Max. 9)			
	8 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	37 $^{\circ}\text{C}$	45 $^{\circ}\text{C}$	8 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	37 $^{\circ}\text{C}$	45 $^{\circ}\text{C}$	8 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	37 $^{\circ}\text{C}$	45 $^{\circ}\text{C}$
0	8.4 $\pm$ 0.3	8.4 $\pm$ 0.4	8.4 $\pm$ 0.3	8.4 $\pm$ 0.4	8.4 $\pm$ 0.4	8.4 $\pm$ 0.4	8.4 $\pm$ 0.4	8.4 $\pm$ 0.5	8.4 $\pm$ 0.4	8.4 $\pm$ 0.4	8.4 $\pm$ 0.3	8.4 $\pm$ 0.4
30	8.3 $\pm$ 0.2	8.2 $\pm$ 0.3	8.1 $\pm$ 0.2	7.9 $\pm$ 0.3	8.3 $\pm$ 0.4	8.2 $\pm$ 0.3	8.1 $\pm$ 0.3	8.0 $\pm$ 0.4	8.3 $\pm$ 0.3	8.2 $\pm$ 0.3	8.1 $\pm$ 0.4	8.0 $\pm$ 0.6
60	8.1 $\pm$ 0.4	8.1 $\pm$ 0.1	7.9 $\pm$ 0.1	7.5 $\pm$ 0.4	8.2 $\pm$ 0.2	8.1 $\pm$ 0.4	8.1 $\pm$ 0.0	7.9 $\pm$ 0.1	8.2 $\pm$ 0.4	8.1 $\pm$ 0.4	8.0 $\pm$ 0.3	7.7 $\pm$ 0.3
90	7.8 $\pm$ 0.3	7.8 $\pm$ 0.3	7.7 $\pm$ 0.3	7.3 $\pm$ 0.1	8.0 $\pm$ 0.3	8.0 $\pm$ 0.3	7.8 $\pm$ 0.1	7.7 $\pm$ 0.3	8.0 $\pm$ 0.5	7.9 $\pm$ 0.6	7.7 $\pm$ 0.5	7.5 $\pm$ 0.4
120	7.7 $\pm$ 0.2	7.6 $\pm$ 0.4	7.5 $\pm$ 0.2	7.1 $\pm$ 0.3	7.8 $\pm$ 0.1	7.8 $\pm$ 0.4	7.5 $\pm$ 0.4	7.3 $\pm$ 0.4	7.9 $\pm$ 0.6	7.8 $\pm$ 0.4	7.5 $\pm$ 0.7	7.2 $\pm$ 0.2
150	7.5 $\pm$ 0.0	7.3 $\pm$ 0.2	7.1 $\pm$ 0.3	6.9 $\pm$ 0.4	7.8 $\pm$ 0.5	7.6 $\pm$ 0.1	7.2 $\pm$ 0.3	6.7 $\pm$ 0.6	7.8 $\pm$ 0.4	7.6 $\pm$ 0.3	7.2 $\pm$ 0.3	6.9 $\pm$ 0.4
180	7.2 $\pm$ 0.5	7.0 $\pm$ 0.3	6.8 $\pm$ 0.1	6.5 $\pm$ 0.4	7.3 $\pm$ 0.3	7.0 $\pm$ 0.2	6.7 $\pm$ 0.2	6.6 $\pm$ 0.5	7.3 $\pm$ 0.5	7.0 $\pm$ 0.4	6.8 $\pm$ 0.4	6.6 $\pm$ 0.1

*n (number of sensory panelists)=7, values expressed as mean $\pm$ SD (n=7)

Table 3 Linear regression analysis ($x \rightarrow y$) between dependent and independent variables

Dependent (Y)	Independent (X)	Slope (m)	Intercept (ln C)	Coefficient of correlation	Coefficient of determination (R^2)
Overall acceptability score	HMF	-0.138	8.288	-0.89	0.809
	TBA value	-6.916	8.190	-0.92	0.847

Arrhenius constant and Q_{10} for the reaction were calculated and found to be 14.60 kJ/mol, 2.190×10^6 Mwk⁻¹ and 1.15, respectively. Change in enthalpy of activation (ΔH) was found in the range of 12.26–14.88 kJ/mol. Free energy of activation (ΔG) was in the range of 67.04–73.85 kJ/mol and entropy of activation (ΔS) for HMF was found to be in the range of -238.54 to -232.22 J/molK for the temperature range from 8 to 45 °C (Table 1).

Increase in TBA value in PM *kheer* mix also followed a first order reaction kinetics. The Arrhenius plot showed a single straight line (Fig. 1d). Polynomial equations were generated to study the change in TBA content at different storage temperatures studied (Table 6). The activation energy, Arrhenius constant and Q_{10} values for the change in TBA value were calculated and found to be 28.70 kJ/mol, 2.912×10^{12} Mwk⁻¹ and 1.53, respectively. Change in enthalpy of activation (ΔH) was found in the range of 26.36–27.98 kJ/mol, free energy of activation (ΔG) was in the range of 67.00–72.11 kJ/mol and entropy of activation (ΔS) for TBA was found to be in the range of -238.35 to -226.68 J/molK for the temperature range from 8 to 45 °C (Table 1).

The activation entropies for all the reactions studied were found to be negative, indicating that activated complex in these reactions are well ordered structures. Increase in storage temperature resulted in a decrease in ΔS for all reactions, suggesting increased randomness of activated complex and increased salvation of the reactants.

Changes in sensory properties of reconstituted PM *kheer* Reconstituted PM *kheer* was subjected to sensory profile analysis (on a 9-point Hedonic scale). The average intensity rating for browning in reconstituted *kheer* increased gradually during storage. Maillard browning was also reflected in increasing HMF values for the *kheer* mix powder during storage. The acceptability of the product in terms of colour scores, correspondingly decreased from

initial 8.4 ± 0.4 to 7.2 ± 0.5 , 8.4 ± 0.4 and 7.0 ± 0.3 , 8.4 ± 0.3 to 6.8 ± 0.1 and 8.4 ± 0.4 to 6.5 ± 0.4 after storage at 8, 25, 37 and 45 °C, respectively. Acceptability of the product in terms of flavour scores, correspondingly decreased from initial 8.4 ± 0.4 to 7.3 ± 0.3 , 8.4 ± 0.4 to 7.0 ± 0.2 , 8.4 ± 0.4 to 6.7 ± 0.2 and 8.4 ± 0.5 to 6.6 ± 0.5 after storage at 8, 25, 37 and 45 °C, respectively. Analysis of variance for statistical analysis of the sensory data exhibited significantly decreased scores after these storage periods ($P < 0.05$).

The combined effect of the decreasing colour and flavour scores of the reconstituted *kheer* from stored *kheer* mix powder as discussed in the preceding sections was that the overall acceptability (hedonic) score declined from 8.4 ± 0.4 (“like extremely”) for the reconstituted fresh product to 7.3 ± 0.5 (close to “like extremely”) for *kheer* mix powder stored at 8 °C for 180 days, 7.0 ± 0.4 (“like very much”) for *kheer* mix powder stored at 25 °C for 180 days, 6.8 ± 0.4 (“like very much”) for *kheer* mix powder stored at 37 °C for 180 days, and 6.6 ± 0.1 (“like very much”) for *kheer* mix powder stored at 45 °C for 180 days (Table 2). The analysis of variance (ANOVA), however, showed that the decline in overall acceptability rating was significant only at 37 and 45 °C, the difference in the product rating becoming larger than the CD after 180 days storage at these temperatures.

Interrelationship between physico-chemical and sensory changes in PM based *kheer* mix The relationship between the physico-chemical and sensory properties of PM *kheer* was done by regression analysis. Linear regression analysis was made between dependent and independent variables. The progression of physico-chemical changes in the product influence the sensory acceptability of the product. The interrelationships between physico-chemical and sensory changes were calculated by linear regression analysis (Table 3). Similarly, interrelationships were made by calculating log-log regression analysis (Table 4).

Table 4 Log-Log (LogX $\rightarrow$ LogY) regression between dependent and independent variables

Dependent (Y)	Independent (X)	Slope (m)	Intercept (ln C)	Coefficient of correlation	Coefficient of determination (R^2)
Overall acceptability score	HMF	-0.131	0.972	-0.944	0.871
	TBA value	-0.111	0.760	-0.933	0.891

Table 5 Polynomial equation for HMF content during storage at different temperatures

Sr. No.	Storage temperature (°C)	Polynomial equation	R ²
1.	8	$y = 0.000x^2 + 0.073x + 4.307$	0.999
2.	25	$y = 0.158x + 4.301$	0.998
3.	37	$y = -0.000x^3 + 0.007x^2 + 0.148x + 4.295$	0.998
4.	45	$y = -4E - 06x^4 + 0.000x^3 - 0.022x^2 + 0.665x + 4.302$	0.999

y=Overall acceptability score
x=HMF

Relationship between overall acceptability score and HMF

The negative correlation between overall acceptability score of PM based *kheer* and HMF of dry mix ($r = -0.944$, $R^2 = 0.871$) could be expressed as under:

$$\text{Overall acceptability} = e^{-0.131 \times e^{\frac{-0.066}{8.314 \times T}} \times t + \text{HMF}} \quad (6)$$

Thus, 87.1 % variation in the overall acceptability score could be explained by increase in HMF content of the dry *kheer* mix (Table 5).

Relationship between overall acceptability score and TBA

The negative correlation between overall acceptability score of PM *kheer* and TBA value of mix ($r = -0.933$, $R^2 = 0.891$) could be expressed as under:

$$\text{Overall acceptability} = e^{-0.111 \times e^{\frac{-0.102}{8.314 \times T}} \times t + \text{TBA}} \quad (7)$$

Thus, 89.1 % variation in the overall acceptability score could be explained by increase in TBA value of dry *kheer* mix (Table 6).

Shelf life prediction models

The kinetic approach to predict the shelf life of any food product requires generation of information relating to the physico-chemical parameters and loss of sensory quality as a function of storage time and temperature. A set of mathematical equations are then developed combining kinetic functions and the functional relationship of variables. The development of mathematical models for predicting shelf life of stored instant PM based dry *kheer* mix was in two steps. In the first step, from among several regression equations described in the preceding section, those with high coefficients of determination ($R^2 = 0.78$ or more) were

selected. It was observed that the overall acceptability score of the product during storage could be best described by change in TBA value. The equations then selected were integrated with the Arrhenius relationship between rate constants and temperature of storage for change in TBA. In view of high correlation coefficient observed between the overall acceptability score and TBA value of instant PM *kheer* mix, the following equation was developed combining the regression of overall acceptability (OA) score on TBA value:

$$\ln(\text{OA}) = \ln C + m[\ln(\text{TBA value}) + A_0 \{e^{-E_a/RT}\}t] \quad (8)$$

Where,

OA overall acceptability score
t time (predicted)
A₀ Arrhenius constant
R gas constant
E_a activation energy
T absolute temperature.

The fitness of this model was tested by calculating root mean square percent (RMS %), as described by Patil and Patel (1992):

$$RMS(\%) = \sqrt{\frac{1}{N} \sum_{i=1}^n \left(\frac{Q_{obs} - Q_{pred}}{Q_{obs}} \right)^2} \times 100 \quad (9)$$

where,

Q_{obs} Observed parametric value
Q_{pred} Predicted parametric value
N Number of observations.

Acceptability of the model developed for predicting overall acceptability on the basis of changes in TBA value was found to be good. Comparison of the predicted values and actual values of OA revealed a high reliability of the model

Table 6 Polynomial equation for TBA content during storage at different temperatures

Sr. No.	Storage temperature(°C)	Polynomial equation	R ²
1.	8	$y = 6E - 06x^2 + 0.002x + .06$	0.998
2.	25	$y = -2E - 05x^2 + 0.004x + 0.060$	0.989
3.	37	$y = 2E - 05x^2 + 0.005x + 0.066$	0.997
4.	45	$y = 1E - 06x^3 - 9E - 05x^2 + 0.011x + 0.069$	0.999

y=Overall acceptability
x=TBA content

as indicated by low values of RMS (0.61, 0.44, 0.35 and 0.24 for 8, 25, 37 and 45 °C, respectively). A shelf life prediction model for instant *kheer* mix was also developed based on changes in HMF content and its regression on overall acceptability score of reconstituted *kheer* (Jha and Patel 2012).

Potential shelf life of PM dry *kheer* mix Above model based on TBA value showing the smallest deviation of the predicted values from the actual values in the range of storage period included in the study was employed to determine the potential shelf life of the product at 8 and 25 °C. For this, assumptions were made that an overall acceptability score of 6.0 for the product would be the minimum acceptable for shelf life determining score and the shelf life model based on data for storage studies of 180 days at 8, 25, 37 and 45 °C would be valid even beyond this period. It was found that the potential shelf life of PM dry *kheer* mix was 396 days at 8 °C and 288 days at 25 °C.

Conclusion

In fresh dry PM *kheer* mix, the average value of HMF recorded was 4.87 µmol/g which increased to 11.23, 13.67, 18.13, and 21.43 µmol/g at 8, 25, 37 and 45 °C, respectively after 180 days of storage. From an initial value of 0.067, the TBA value increased to 0.219, 0.311, 0.432 and 0.613 at 532 nm at 8, 25, 37 and 45 °C, respectively after 180 days of storage. Changes in HMF and TBA followed first order reaction kinetics. Rate constants for these changes were found to be temperature dependent. The overall acceptability score of PM based *kheer* showed significant ($p < 0.01$) negative correlation with TBA value for the dry mix packaged under nitrogen flushing conditions. So the relevant regression equations were integrated with the corresponding Arrhenius relationship in order to develop shelf life prediction model. Shelf life of dry PM *kheer* mix worked out to be 396 and 288 days at 8 and 25 °C, respectively under nitrogen flushing conditions.

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