A study on degradation kinetics of thiamine in red gram splits (*Cajanus cajan* L.)

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Abstract

The kinetics of thiamine degradation in red gram splits (*Cajanus cajan* L.) as well as in pure thiamine solutions (at initial concentrations present in red gram splits) have been studied at pH 4.5, 5.5 and 6.5, over a temperature range of 50–120 °C (steady state temperature process). The degradation kinetics of thiamine, in normal open pan cooking, pressure-cooking and a newly developed and patented fuel-efficient 'eco- cooker', have also been studied (unsteady state heating process). The thiamine degradation was observed to follow first order kinetics where the rate constant increased with an increase in the temperature. The temperature dependence of degradation was adequately modelled by the Arrhenius equation. A mathematical model has been developed, using the steady state kinetic parameters obtained, to predict the losses of thiamine from the time-temperature data of the unsteady state heating/cooking process. The results obtained indicate a thiamine degradation of similar magnitude in all the three modes of cooking used in the study.

Keywords: Thiamine degradation; Kinetics; Red gram splits; Cookers

1. Introduction

Knowledge of degradation kinetics, including reaction order, rate constant and activation energy, is essential to predict food quality loss during storage as well as thermal processing. One of the important factors to be considered in food processing is the loss of nutrients. Water-soluble vitamins, especially thiamine are known to be sensitive to processing conditions (especially temperature and pH) e.g. in cooking and baking of meats, vegetables, and fruits and during storage (Bender, 1966). Thiamine is found in foods in the free form or in a combined form as a protein-complex or pyrophosphoric acid ester–co-carboxylase (Mulley, Stumbo, & Hunting, 1975a, 1975b). The stability is affected by pH, temperature, heating time, water activity or moisture content, ionic strength, buffer type and processing method (Belitz & Grosch, 1999; Bender, 1966; Feliciotti & Esselen, 1957; Steaven, 1988; Steaven, Veron & Michael, 1985). Stability of thiamine is also affected by some food components. It is reported that starch and/or proteins decrease thiamine loss during processing (Basant & Roy, 1973; Steaven, 1988; Steaven et al., 1985).

Many studies have been reported on the degradation of thiamine with respect to different conditions and systems. An early report by Feliciotti and Esslen (1957) on the heat-sensitivity of thiamine in aqueous, buffered solutions, and in eight low-acid foods over a temperature range of 109–149 °C, indicated it to be more resistant to thermal breakdown in foods than in pure aqueous or buffered solutions. An increase of water activity decreases the rate of thiamine degradation (Fernendez, Murai, Resnik & Tomio, 1986; Abrabshahi & Lund, 1988). Nitrites, sulfur dioxide and sulfites can cause loss of thiamine during processing and storage (Basant & Roy, 1973; Belitz & Grosch, 1999; Pizzareto, 1991). Studies conducted by Watanabe and Ciacco (1990) on the influence of processing and cooking on the retention of nutrients in spaghetti revealed thiamine loss to be greater than riboflavin or niacin.

Degradation of thiamine in aqueous and buffered solutions is reported to follow first order reaction kinetics (Farrer, 1955; Feliciotti, 1957). Mulley, Stumbo, and Hunting (1975a, 1975b) studied the rates

of thiamine destruction in phosphate buffer (pH 6), and in selected low-acid foods, such as pea puree, beef puree and peas, in brine over a temperature range of 121–138 °C. Higher stability of thiamine in food systems then in phosphate buffer was established. These workers tried to elucidate the effect of pH, in the range 4.5–6.5, on vitamin destruction. At all pH values, the reaction followed first order kinetics, and the stability of thiamine decreased with increase in pH. Farrer (1955) suggested that, in meats, the main variable effecting thiamine destruction is likely to be the proportion of co-caboxylase present. However, Mulley, Stumbo, and Hunting (1975a 1975b) reported that co-caboxylase, at levels found in foods, would not influence the degradation of thiamine.

Studies on the effect of γ-irradiation on thiamine stability have been reported (Fox et al., 1997). Low dose γ-irradiation of vacuum-packed ground fresh pork resulted in dose-dependent first order rate of thiamine destruction. Doses greater than 0.75 kGy resulted in considerable destruction of thiamine (Jenkins, Thayer, & Hansen, 1989). The loss of thiamine due to irradiation ranges from 3 to 34% (Fox, Lakrits, Hampson, Richardso, Ward, & Thayer, 1995). Thiamine degradation during extrusion is reported to follow first order kinetics, with the kinetic rate constant dependent on the product temperature, feed moisture and screw speed (Ilo & Berghofer, 1998).

Most studies on degradation kinetics of thiamine deal only with higher temperature ranges. Different processing methods are used in usual household cooking. Some of them are normal open pan cooking, pressure cooking, and slow cooking. A fuel-efficient cooker has been recently developed in our institute (Joshi & Patel, 2000). The principle of this cooker is based on multiple effect evaporation, slow heating proportional to pick up rate of heat by the cooking vessel, and insulation, and on the logic of combining these principles in one unit. A literature survey, done over the past 60 years, did not give any information on the degradation kinetics of nutrients in foods cooked at different rates, particularly those used on the Indian subcontinent, such as cereals, pulses and legumes. A scan of the nutrient composition in various grains and legumes showed red gram (Cajanus cajan L.), also known as pigeon pea, to be a rich source of thiamine (Gopalan, Sastri, & Balasubramanian, 1996). It is an important grain legume, which is grown and consumed in the tropics and semi-arid tropics of the world (Singh, 1988). India accounts for about 90% of the world supply of red gram. It is also grown in East Africa and South East Asian countries (Singh, Jambunathan, Saxena, & Subrahmanyan, 1990). Red gram is a rich source of protein, thiamine, riboflavin, niacin, folic acid and minerals such as calcium and iron (Meiners et al., 1976). Hence it was selected as a model food system for

studying the degradation kinetics of thiamine. Red gram is usually consumed in three different forms—as plain red gram curry (pH ∼ 6.5), as red gram cooked along with tomatoes (pH ∼ 5.5), and as 'sambar' in which tamarind pulp is added (pH ∼ 4.5). Hence the studies were done at pH 4.5, 5.5 and 6.5.

The main objectives of the present study were to (1) to determine the kinetic parameters for thiamine degradation red gram splits (Cajanus cajan L.), a model Indian food ingredient, as well as pure solution of thiamine at concentration found in the red gram splits over a temperature range of 50–120 °C (steady state temperature) at pH 6.5, 5.5 and 4.5; (2) to study the degradation kinetics of thiamine for different cooking methods at the selected pH (unsteady state process); (3) to develop a mathematical model relating the calculated kinetic data from the steady state temperature and time temperature profiles of different cooking methods (unsteady state process); (4) to apply this model to predict thiamine degradation for the unsteady state heating process, from the time temperature data of the unsteady state heating process and comparison with the actual degradation values, which could then be used to asses the nutritional values as a function of method of cooking.

2. Materials and methods

2.1. Materials

Red gram splits were procured from the market. Thiamine hydrochloride was obtained from S.D. Fine Chemicals, Mumbai. The pH of the water was adjusted using 1N HCl.

2.2. Heat treatment

Heat treatments were carried out at different temperatures (50, 60, 70, 80, 90,100 and 120 °C) for 0–60 min. A water bath was used as a heating device for temperatures up to 100 °C while, for 120 °C, an autoclave was used. To study the effect of other constituents of red gram splits on degradation of thiamine, degradation kinetics of pure thiamine at concentration found in the same were also studied. 10 g of red gram splits were transferred into a 100 ml beaker containing 30 ml distilled water pre-heated to the desired time/temperature conditions, and immediately analyzed for thiamine using the fluorimetric method (AOAC, 1984; Fernendez et al., 1996; Taungbodhitham, 1995).

2.3. Cooking methods

For cooking studies, normal open pan cooking (30 min at a gas flow rate of 15 ml/s), pressure-cooking

(15 min at 15 ml/s) and the newly developed slow cooker, named 'eco cooker' (30 min at sim, that is at a gas flow rate of 6 ml/s and 30 min holding period) were selected as different cooking methods. The time and flow rates for open pan and pressure- cooking were selected according to the protocol used in household practices that ensure complete cooking of the red gram splits. The time and flow rates for the 'eco cooker' were selected the instructions given for its usage (Joshi & Patel, 2000). The samples were taken out periodically and analyzed for thiamine. A 1:3, w/v, ratio of the splits to water was cooked as above in the three modes of cooking.

2.4. Time-temperature data

Time-temperature data for each cooking method were monitored using a thermocouple.

2.5. Determination of thiamine

Thiamine was analyzed using the procedure described by AOAC (1984). For the determination of thiamine, 10g red gram splits were transferred a 100 ml beaker containing 30 ml distilled water pre-heated to the desired time/temperature conditions. After the heat treatment(s), samples were taken out immediately and 50 ml of 0.2N HCl added. Samples were then heated on a boiling water bath for 30 min, made up to 100 ml and filtered. 25 ml of the filtrate were then loaded onto a Decalso column and eluted with acid potassium chloride solution. Eluted thiamine was then oxidized to thiochrome with alkaline potassium ferricyanide. The fluorescent intensity of thiochrome extracted with iso-butanol was determined in a luminescence spectrometer (Perkin Elmer, LS 30) at an excitation wavelength of 360 nm and an emission wavelength of 435 nm. Thiamine was read from a standard curve prepared using standard thiamine in the range 0.0–0.5 µg.

For pure thiamine solutions, heat treatments were carried out as above. Samples were removed and then further oxidized to thiochrome. The purification step was eliminated here. Amount of thiamine was determined as described above.

The accuracy of the analytical method was confirmed by conducting the following experiment; 100 g of redgram splits were added to 300 ml distilled water (pH–6.5) at 100 °C. The mixture was held for 60 min at 100 °C. After 60min, it was macerated in a mixer-grinder to get uniform consistency. It was then divided into eight samples of 40 g each. The amount of thiamine was estimated as described above. Thiamine concentration was found to be 0.10875 ± 0.000968 mg/100 g and the accuracy of the analytical procedure was found to be 99.1%. Thus, the thiamine concentration, over the range studied in this work, could be estimated within $\pm 1\%$ accuracy.

2.6. Kinetic calculations

A general reaction rate expression for the degradation kinetics can be written as follows (Libuza & Riboh, 1982; Van Boekel, 1996; Ramaswami, Van De Voort, & Ghasal, 1989).

$$-\mathrm{d}[C]/\mathrm{d}t = k[C]^m \qquad (1)$$

where 'C' is the quantitative value of the product of degradation under consideration, 'k' is the reaction rate constant, and 'm' is the order of the reaction. The equation for first order kinetics after integration of Eq. (1) can be written as:

$$\mathrm{Ln}([C_t]/[C]0) = -kt \qquad (2)$$

where '$[C]_0$' is the value of the product under consideration at time 0, and '$[C]_t$' is the value after reaction time 't'.

The relationship of reaction rate to temperature was quantified by the Arrhenius relationship.

$$k = A0\exp(-E_a/RT) \qquad (3)$$

where 'E_a' is the activation energy of the reaction, 'R' is the gas constant, 'T' is absolute temperature, and 'A_0' is a pre-exponential constant.

Each experiment was done in triplicate and average values were taken for the analysis. Kinetic data were analyzed by regression analysis, using MS Excel.

3. Results and discussion

3.1. Concentration of thiamine in red gram splits after the time-temperature treatments as indicated

Tables 1–3 show the concentration of thiamine after heat treatments at 50–120 °C for different time periods at pH 6.5, 5.5 and 4.5 respectively, while Tables 4–6 show similar data for thiamine solution containing thiamine at 0.38 mg/100 ml (the concentration found in red gram splits in the present study). It can be seen that thiamine is more stable in red gram splits than in the pure solutions. This observation is in accordance with earlier reports (Feliciotti & Esslen, 1957). Red gram is a good source of starch and proteins, two constituents that are reported to exert protective effect on thiamine degradation (Basant & Arnold, 1973; Belits & Grosch, 1999; Steavan, 1989).

3.2. Kinetic data for degradation of thiamine in red gram splits and pure thiamine solution at pH 6.5, 5.5 and 4.5

In order to arrive at kinetic data, a first order degradation was presumed. Accordingly, '$\mathrm{Ln}([C]_t/[C]_0)$' was plotted vs 't', from which rate constant, 'k', was calculated

Table 1
Effect of heating on thiamine concentration (mg/100 g) in redgram splits (pH 6.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.257±0.003
10	0.380±0.004	0.380±0.009	0.354±0.001	0.342±0.002	0.329±0.006	0.299±0.001	0.194±0.008
15	–	–	–	–	–	–	0.157±0.008
20	0.379±0.001	0.361±0.005	0.327±0.008	0.298±0.005	0.264±0.005	0.235±0.002	0.137±0.001
30	0.368±0.004	0.345±0.002	0.302±0.005	0.257±0.004	0.222±0.001	0.169±0.002	–
40	0.354±0.003	0.340±0.003	0.290±0.004	0.241±0.005	0.198±0.002	0.149±0.005	–
50	0.342±0.002	0.327±0.005	0.270±0.006	0.231±0.002	0.189±0.006	0.126±0.006	–
60	0.340±0.0001	0.315±0.003	0.260±0.005	0.224±0.003	0.170±0.005	0.109±0.001	–

Values are means±S.D. of three or more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.

Table 2
Effect of heating on thiamine concentration (mg/100 g) in redgram splits (pH 5.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.287±0.005
10	0.380±0.004	0.370±0.001	0.367±0.002	0.350±0.008	0.340±0.009	0.325±0.005	0.246±0.003
15	–	–	–	–	–	–	0.178±0.007
20	0.365±0.002	0.365±0.004	0.348±0.005	0.328±0.004	0.315±0.005	0.300±0.008	0.150±0.006
30	0.36±±0.006	0.354±0.003	0.328±0.006	0.300±0.005	0.281±0.004	0.270±0.005	–
40	0.355±0.007	0.341±0.006	0.301±0.005	0.284±0.006	0.270±0.002	0.225±0.006	–
50	0.345±0.007	0.329±0.009	0.292±0.003	0.269±0.004	0.225±0.005	0.175±0.009	–
60	0.335±0.003	0.312±0.005	0.270±0.008	0.245±0.005	0.200±0.009	0.145±0.008	–

Values are means±S.D. or three of more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.

Table 3
Effect of heating on thiamine concentration (mg/100 g) in redgram splits (pH 4.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.3±0.009
10	0.380±0.001	0.380±0.004	0.368±0.004	0.357±0.003	0.342±0.004	0.321±0.005	0.256±0.008
15	–	–	–	–	–	–	0.230±0.006
20	0.380±0.005	0.375±0.009	0.350±0.008	0.332±0.004	0.320±0.009	0.299±0.003	0.171±0.005
30	0.370±0.006	0.370±0.008	0.330±0.006	0.316±0.005	0.293±0.005	0.240±0.004	–
40	0.360±0.009	0.353±0.003	0.312±0.004	0.291±0.008	0.275±0.006	0.216±0.008	–
50	0.353±0.004	0.340±0.008	0.301±0.009	0.279±0.003	0.246±0.005	0.180±0.002	–
60	0.344±0.003	0.320±0.004	0.289±0.006	0.245±0.005	0.218±0.005	0.149±0.003	–

Values are means±S.D. of three or more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.

Table 4
Effect of heating on thiamine concentration (mg/100 ml) in pure solution (pH 6.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.310±0.008
10	0.374±0.001	0.358±0.005	0.350±0.002	0.340±0.001	0.330±0.002	0.300±0.002	0.240±0.004
15	–	–	–	–	–	–	0.172±0.003
20	0.369±0.002	0.346±0.003	0.341±0.009	0.319±0.006	0.304±0.011	0.264±0.002	0.104±0.006
30	0.360±0.0020	0.340±0.002	0.330±0.003	0.304±0.005	0.278±0.008	0.209±0.001	–
40	0.350±0.009	0.327±0.004	0.310±0.001	0.270±0.001	0.239±0.005	0.149±0.009	–
50	0.338±0.001	0.315±0.004	0.296±0.002	0.235±0.007	0.210±0.007	0.129±0.005	–
60	0.323±0.009	0.300±0.008	0.285±0.002	0.217±0.001	0.167±0.020	0.080±0.008	–

Values are means±S.D. of three or more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.

Table 5

Effect of heating on thiamine concentration (mg/100 ml) in pure solution (pH 5.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.281±0.004
10	0.380±0.006	0.370±0.003	0.355±0.005	0.340±0.006	0.330±0.007	0.308±0.007	0.230±0.008
15	–	–	–	–	–	–	0.170±0.009
20	0.370±0.005	0.365±0.005	0.341±0.004	0.321±0.002	0.300±0.006	0.271±0.004	0.147±0.006
30	0.360±0.003	0.360±0.008	0.318±0.008	0.290±0.003	0.272±0.005	0.230±0.006	–
40	0.355±0.003	0.340±0.003	0.290±0.004	0.271±0.007	0.260±0.004	0.205±0.008	–
50	0.340±0.004	0.325±0.004	0.281±0.005	0.252±.004	0.213±0.004	0.160±0008	–
60	0.320±0.004	0.305±0.005	0.270±0.001	0.220±.007	0.186±0.006	0.128±0.009	–

Values are means±S.D. of three or more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.

Table 6

Effect of heating on thiamine concentration (mg/100 ml) in pure solution (pH 4.5) at various temperatures

Time (min)	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	120 °C
5	–	–	–	–	–	–	0.291±0.004
10	0.380±0.009	0.380±0.004	0.365±0.005	0.342±0.006	0.340±0.009	0.310±0.006	0.229±0.005
15	–	–	–	–	–	–	0.180±0.006
20	0.372±0.006	0.370±0.007	0.352±0.009	0.326±0.004	0.32±0.003	0.282±0.007	0.160±0.009
30	0.365±0.007	0.352±0.003	0.328±0.004	0.304±0.005	0.292±0.005	0.220±0.006	–
40	0.354±0.003	0.348±0.006	0.310±0.007	0.282±0.003	0.270±0.004	0.191±0.009	–
50	0.340±0.004	0.330±0.009	0.298±0.006	0.260±0.005	0.230±0.005	0.161±0.005	–
60	0.330±0.003	0.310±0.007	0.281±0.006	0.245±0.007	0.198±0.003	0.133±0.006	–

Values are means±S.D. of three or more individual determinations. The thiamine content of the redgram splits chosen in the study was 0.38 mg/100 g.
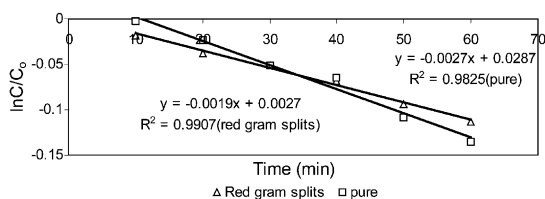

Fig. 1. First order plot of thiamine degradation in splits and in pure solution at 50 °C.
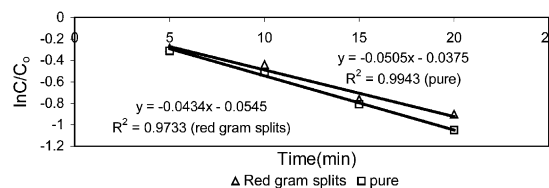

Fig. 3. First order plot of thiamine degradation in splits and in pure solution at 120 °C.
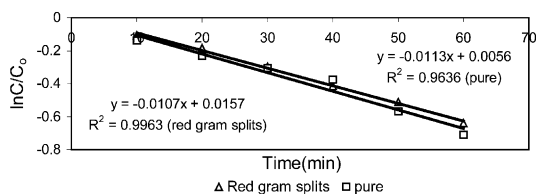

Fig. 2. First order plot of thiamine degradation in splits and in pure solution at 100 °C.

as the slope. Figs. 1–3 show the representative plots for red gram splits and pure thiamine solution at pH 5.5 at 50, 80 and 120 °C, respectively. A correlation coefficient, > 0.9 in all cases, confirmed that the degradation followed first order kinetics. Similar data were obtained at all the temperatures for the three pH values chosen in this work. $t_{1/2}$, the time required for thiamine to degrade to 50% of its original value was calculated from the rate constant as '0.693/k'. Tables 7 and 8 document the rate

constants and '$t_{1/2}$' (min) for thiamine in red gram splits and in pure solutions. It is evident from these Tables that the rate of thiamine degradation decreased with decrease in pH. As the pH decreased from 6.5 to 4.5, the rate constant for thiamine degradation in red gram decreased from 0.0027 to 0.0019 min^{-1} at 50 °C and 0.0418 to 0.0398 min^{-1} at 120 °C. Under similar conditions of pH, the rate constant for thiamine degradation in red gram splits and pure solution was marginally different up to 80 °C. However, at 90 °C and above, the rate constant for thiamine degradation was lower in red gram splits than in pure solutions. These observations confirm the protective effect of red gram constituents on thiamine degradation, and are in agreement with earlier reports (Farrer, 1957; Feliciotti & Esselen, 1957; Mulley, Stumbo, & Hunting, 1975a 1975b).

Activation energies E_a, (cal M^{-1}) were calculated as a product of gas constant, R (1.987 cal M^{-1} K^{-1}) and the

Table 7
Rate constant k', correlation coefficient (R^2) and half-life ($t_{1/2}$) of thiamine degradation in red gram redgram splits at pH 6.5, 5.5 and 4.5

Temperature (°C)	pH 6.5			pH 5.5			pH 4.5		
	k (min^{-1})	R^2	$t_{1/2}$ (min)	k (min^{-1})	R^2	$t_{1/2}$ (min)	k (min^1)	R^2	$t_{1/2}$ (min)
50	0.0027	0.95	256.6	0.0019	0.99	345	0.0019	365	0.95
60	0.0036	0.99	192.0	0.0034	0.97	204	0.0033	210	0.92
70	0.0060	0.98	115.0	0.0061	0.98	114	0.0049	141	0.99
80	0.0100	0.92	69.00	0.0069	0.99	100	0.0068	102	0.97
90	0.0120	0.92	58.00	0.0107	0.99	65	0.0089	78	0.99
100	0.0200	0.97	35.00	0.0167	0.97	41	0.0156	44	0.99
120	0.0418	0.98	16.50	0.0454	0.97	15	0.0398	17.4	0.97

Table 8
Rate constant k', correlation coefficient (R^2) and half-life ($t_{1/2}$) of thiamine degradation in pure thiamine solution at pH 6.5, 5.5 and 4.5

Temperature (°C)	pH 6.5			pH 5.5			pH 4.5		
	k (min^{-1})	R^2	$t_{1/2}$ (min)	k (min^{-1})	R^2	$t_{1/2}$ (min)	k (min^{-1})	R^2	$t_{1/2}$ (min)
50	0.027	0.96	25.60	0.0027	0.98	257	0.0026	0.97	267
60	0.031	0.99	22.35	0.0039	0.94	178	0.0038	0.96	182
70	0.036	0.99	19.25	0.0065	0.94	107	0.0054	0.97	128
80	0.045	0.97	15.40	0.0085	0.99	82	0.0075	0.99	92
90	0.060	0.96	11.50	0.0113	0.96	61	0.0108	0.97	64
100	0.080	0.95	08.66	0.0173	0.98	40	0.0176	0.99	39
120	0.125	0.98	05.54	0.0500	0.99	14	0.0408	0.98	17
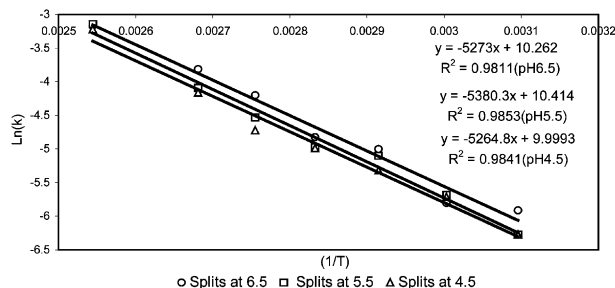
Fig. 4. Arrhenius plot for thiamine degradation in red gram splits at pH 6.5, 5.5 and 4.5.

Fig. 5. Time–temperature profiles of the different cooking method used.

slope of the graph obtained by plotting 'Ln k' vs '$1/T$'. Fig. 4 shows the Arrhenius plot for thiamine degradation in red gram splits at pH 6,5, 5.5 and 4.5. The linear natures of the plots obtained indicate thermal destruction of thiamine to conform to the Arrhenius equation. The activation energies of thiamine in red gram splits were found to be 9.45, 10.7 and 9.82 kcal/ mole at pH 4.5, 5.5 and 6.5, respectively. There is not much difference between the activation energies under different conditions of pH, suggesting similar mechanism of degradation in all cases.

3.3. Time–temperature data of the three modes of cooking

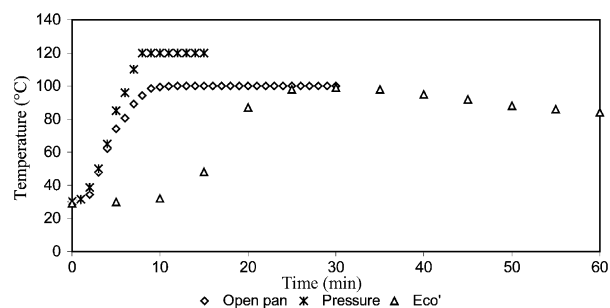To extend the results obtained from steady state experiments to the unsteady state encountered in the three modes of cooking, i.e. open pan cooking, pressure cooking and cooking in the 'Eco cooker', time–temperature data during the processing of each were recorded (Fig. 5).

3.4. Degradation profile and half life values of thiamine in red gram splits under the three modes of cooking

Thiamine degradation was followed in each of these modes of cooking as for red gram splits under steady state conditions. The results documented in Table 9 indicate that thiamine is more stable at lower pH as can be seen from the half-life values. Thiamine retention was of a similar order of magnitude in all modes of cooking used in the study, though some minor effect of the pH was observed. Since the extent of degradation

Table 9
Degradation profile and kinetics of thiamine degradation in red gram splits by three methods of cooking

Time of Cooking (min)	Method of Cooling								
	Open pan cooking[a]			Pressure cooking[a]			Eco' cooking[a,c]		
	pH 6.5	pH 5.5	pH 4.5	pH 6.5	pH 5.5	pH 4.5	pH 6.5	pH 5.5	pH 4.5
5	–	–	–	0.361 ± 0.007	0.361 ± 0.003	0.367 ± 0.003	–	–	–
10	0.338 ± 0.005	0.352 ± 0.004	0.358 ± 0.009	0.260 ± 0.005	0.32 ± 0.005	0.329 ± 0.006	0.362 ± 0.007	0.368 ± 0.004	0.369 ± 0.009
15	–	–	–	0.218 ± 0.008	0.238 ± 0.007	0.243 ± 0.003	–	–	–
20	0.290 ± 0.008	0.31 ± 0.007	0.321 ± 0.004	–	–	–	0.308 ± 0.006	0.339 ± 0.009	0.349 ± 0.008
30	0.232 ± 0.006	0.249 ± 0.006	0.255 ± 0.005	–	–	–	0.160 ± 0.004	0.21 ± 0.008	0.231 ± 0.003
K[b]	0.0188	0.0176	0.017	0.0504	0.0417	0.0142	0.0408	0.028	0.0239
(R^2)	(0.99)	(0.98)	(0.96)	(0.97)	(0.93)	(0.93)	(0.86)	(0.86)	(0.84)
$T_{1/2}$ (min)	36.86	40.1	41.0	14.0	17.0	17.0	17.0	25.0	29.0

[a] Results are mean ±S.D. of three determinations.
[b] Calculated from semi-log plot of Ln C_0/C_t vs t.
[c] Held for 30 min according to the protocol recommended for cooking with 'Eco cooker'.

Table 10
The actual and predicted retention of thiamine (mg/100 g or mg/100 ml)in the cooking methods

Cooking method		Redgram redgram splits (4.5)[a]	Redgram redgram splits (5.5)[a]	Redgram redgram splits (6.5)[a]
Open pan	Actual	0.255	0.249	0.232
	Predicted	0.261	0.238	0.230
Pressure cooking	Actual	0.240	0.238	0.278
	Predicted	0.289	0.263	0.262
Eco' cooking	Actual	0.229	0.210	0.160
	Predicted	0.213	0.186	0.175

[a] pH.

observed was much more than the measurement accuracy ($\pm1\%$), all the reported values in Table 9 can be considered to have a 99% confidence limit.

3.5. Prediction of thiamine loss during unsteady state heating processing

To predict the amount of thiamine degradation occurring in red gram splits during a given unsteady state heating process, the following equation was derived from the integrated first order rate law.

$$k_i = A_0 \exp(-E_a/RT_i) \qquad (4)$$

where 'k_i' is the rate constant at time 't_i'. 'E_a' is the activation energy of the reaction, 'R' is the gas constant, 'T' is absolute temperature, and A_0 is a pre-exponential constant, already calculated for the steady state heating process. The rate constant 'k_i' at each temperature, was calculated using Eq. (4) substituting for T from the time temperature data of the unsteady state heating process. Knowing the rate constant k_i, the rate dC/dt_i, the amount degraded during the time interval zero to t_i and the final concentration 'C' can be calculated as follows:

Rate = Rate constant $k_i \times$ Initial concentration C.
Amount degraded during t_i (ΔC) = Rate $\times$ t_i
Concentration after time t_i = $C - \Delta C$.

These calculations were continued for the entire time period (heating and constant temperatures) during which each cooking process was done. An MS excel-based computer programme was used to calculate the above parameters.

The total amount degraded after complete cooking = $\Sigma \Delta C$. The final concentration will thus be = $C_0 - \Sigma \Delta C$, where C_0 is the initial concentration of thiamine. The resulting predictions and the actual degradation obtained experimentally are given in Table 10. As seen, a good agreement between the actual and the predicted degradation/retention of thiamine was obtained. Using this method, the degradation of thiamine can be predicted for any processing method, if the time-temperature profile of that processing operation is known.

4. Conclusions

Slow cookers, as exemplified by the 'Eco cooker', although fuel-efficient, show no significant difference in

the magnitude of retention as compared to normal open pan and pressure cooking at all the pH values studied in this work. The need to study the retention of other water-soluble vitamins is also warranted. Based on the nutrient retention, in this particular case thiamine, and fuel savings, an overall judgment in favour of the slow 'Eco cooker' is suggested.

Acknowledgements

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