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The degradation kinetics of flavor in black pepper (*Piper nigrum* L.)

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ABSTRACT

Kinetics of flavor degradation in black pepper was studied at isothermal (50–120 °C) and non-isothermal conditions. The degradation of flavor was also followed in three different cooking methods viz., open pan, pressure cooking and a newly developed slow cooker named "EcoCooker'. Flavor was evaluated in terms of piperine for pungency and total extractable oleoresin. The degradation of flavor (piperine and total extractable oleoresin) was found to follow first order kinetics. A mathematical model has been developed using the isothermal kinetic parameters obtained to predict the flavor loss from the time–temperature data of non-isothermal heating/processing method.

1. Introduction

Foods however nutritious are not appreciated without good flavor. Flavor is a most important characteristic property, which governs the acceptability of any food product. Spices form a class of their own in natural flavors. Pepper from *Piper nigrum* L. is one of the oldest and worlds most important spices (Purseglove et al., 1981), which is also known as the 'king of spices' or even as 'black gold'. Different products from black pepper available are ground pepper, pepper oil and oleoresin (Ravindran and Johny, 2001). Pepper is associated with a number of functional properties such as analgesic and antipyretic properties, antioxidant effects and antimicrobial properties (Kapoor et al., 1993). Piperine, an active ingredient in pepper, exerts substantial analgesic and antipyretic effects (Lee et al., 1984).

Pepper is an important ingredient in many flavoring and seasoning formulations all over the world. Ground pepper, produced by grinding dried white or black pepper in a hammer mill affects the volatile oil. Storage experiment on ground pepper revealed losses of α-pinene limonene and 3-methyl butanal to be mainly responsible for deficit in pepper like note after 30 days of storage at room temperature (Ravindran and Johny, 2001). Chacko et al. (1996) conducted some experiments on the effects of heating on the flavor profile of black pepper (*P. nigrum*) where black peppercorns were heated at 100–150 °C for 15 or 30 min in either a conventional or a microwave oven in order to simulate dry roasting. It was demonstrated that volatile oil yields and contents of oleoresin and piperine were generally unaffected by heating whereas some improvement in aroma of heated pepper was noted, with oven heated samples receiving better sensory scores than microwave heated samples. GC and GC MS analysis showed that heating resulted in changes in relative composition of major components such as limonene, pinenes, sabinene, caryophyllene, etc., which may be responsible for the changed flavor profile.

There are contradictory reports available with respect to heat stability of piperine during cooking. Traditionally, spices especially pepper powder is generally added at the end of cooking in order to avoid losses of heat sensitive pepper flavor and pungency. The loss off piperine during cooking of a traditional Indian curry preparation called *rasam*, for 15 min/30 min was reported (Srinivasan et al., 1992). The black pepper was added as a part of curry powder and as pure black pepper powder in *rasam* preparation at pH 5.1 and 6.1. The loss of piperine during cooking was in the range of 53–62% when black pepper was used as a part of curry powder, and the pH did not make any difference to the extent of piperine loss. But the loss of piperine was 13–17% and 49–54% at pH 6.1and 5.1 respectively when pure black pepper powder was used as spice ingredient. The loss of Piperine in black pepper during heat processing (boiling for 10 and 20 min and pressure cooking for 10 min) were in the range 27–34% with maximum loss being observed in pressure cooking (Suresh et al., 2007).

Pepper is an essential ingredient of most curry powders used in cooking all over the world, but most extensively used in Indian as

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well as South Asian cooking (Ravindran and Johny, 2001). There are no data on kinetics of flavor loss/degradation of pepper either at static conditions of fixed temperatures, or under dynamic changing temperatures during different cooking methods. Therefore the present study was undertaken with a view (1) to find the kinetic parameters of flavor degradation in black pepper powder (*P. nigrum* L.), during isothermal conditions (over a temperature range of 50–120 °C) and non-isothermal conditions (cooking) and (2) to develop a mathematical model from the kinetic data obtained from (1) and to apply this model to predict the flavor degradation in black pepper for any non-isothermal process.

2. Materials and methods

Black pepper (*P. nigrum* L, var. Malbar) was obtained from Spice Board of India, Kerala, India. Standard piperine was procured from M/s Sigma Chemical Co., St. Louis; USA. All chemicals used were of Analytical Reagent grade.

2.1. Sample Preparation

Black pepper was ground in a grinding mixer (M/s Kenstar Super, model no. MG 9802, Mumbai, India) to pass through sieve of 60–80 mesh.

2.2. Heat treatment

Heat treatments were carried out at different temperatures (50, 60, 70, 80, 90, 100, 110 and 120 °C) for 0–60 min. The temperatures were measured with ±0.1 °C accuracy and the come up time was less than a minute. A water bath (Tempo instruments & equipments, Mumbai, India) was used as a heating device for temperatures up to 100 °C, while for 120 °C an autoclave was used so as to maintain a temperature of 120 °C during heat treatment. The come up time for all the cooking method was less than 5 min. Five grams of accurately weighed ground black pepper was mixed with 30 ml water in a 100 ml beaker and heated at predetermined temperature–time, with frequent stirring. Samples were withdrawn periodically and content of piperine and pepper oleoresin was determined as described in Section 2.4.

2.3. Cooking methods

For cooking studies normal open pan cooking (30 min at a gas flow rate of 15 ml/s), pressure cooking (20 min at a gas flow rate of 15 ml/s) and one newly developed slow cooker (Joshi and Patel, 2002) named 'EcoCooker' (30 min at a gas flow rate of 6 ml/s and 30 min holding period) were selected as different cooking methods. The principle of 'EcoCooker' 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.

2.4. Analysis of flavor

Flavor was quantified in terms of piperine content of black pepper powder and extractable oleoresin (volatiles + nonvolatile) from the black pepper powder.

2.4.1. Quantification of piperine in black pepper

The heat treated samples were extracted with 10 volumes chloroform for 1 h under dark in a shaker, filtered and 0.1 ml of this was made up to 10 ml with chloroform; 0.1 ml of this solution was again taken in a 10 ml volumetric flask and made up to volume with chloroform. Optical density was then measured at 343 nm using UV spectrophotometer (Fagen et al., 1955; Tausig et al., 1956; Genest et al., 1963; Shaikh et al., 2006). The piperine percent in black pepper was calculated from previously plotted standard graph using pure piperine with concentration ranging between 0 and 125 ppm. The regression equation correlating the OD at 343 nm and piperine content is $y = 12508x$ ($R^2 = 0.999$)

2.4.2. Quantification of extractable black pepper oleoresin

The heat treated sample of black pepper powder in water was filtered. The residue was extracted in a soxhlet apparatus using alcohol for 10–12 h. The extract was cooled, filtered through a bed of Na_2SO_4 for removal of moisture. It was then concentrated by heating in water bath under vacuum of 25' Hg in a rotavac; the temperature maintained was 60–65 °C for alcohol extract. The concentration was carried out until the extract was devoid of solvent odor. The extract was collected in glass bottles and weighed to determine the yield.

2.5. Kinetic calculations

A general reaction rate expression for the degradation kinetics can be written as follows (Van Boekel, 1996; Nisha et al., 2004).

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

where '*C*' is the quantitative value of the component under consideration, '*k*' is the reaction rate constant, and '*m*' is the order of the reaction. Data were analyzed according to the first order kinetic equation:

$$\ln(C_t/C_0) = -kt \tag{2}$$

The dependence of the degradation rate constant (k_T) on temperature was quantified by the Arrhenius equation, where

$$k_T = A_0 \exp(-E_a/RT) \tag{3}$$

where C_0 is the initial concentration of piperine; C_t is the concentration at time 't'; *t* is the heating time (min); E_a is the activation energy of the reaction (kJ mol^{-1}); *R* is the universal gas constant (8.3145 J mol^{-1} K^{-1}); *T* is the absolute temperature (K); A_0 is the frequency factor (min^{-1}) is a pre-exponential constant.

Each experiment was done in triplicate. Kinetic data were analyzed by linear regression analysis using MS Excel.

3. Results and discussion

3.1. Effect of temperature on flavor (piperine and oleoresin) of pepper

Table 1 shows the effect of heat treatment on the piperine and oleoresin content of pepper powder. As can be seen, oleoresin was found to be stable at 50 °C and there was no loss of at temperatures 50 and 60 °C. This difference may be because the volatile compounds being heat sensitive are getting evaporated at lower temperatures, whereas piperine is more stable at those temperatures. The losses were found to be faster at higher temperature for piperine as well as for oleoresin.

3.2. Kinetic data for degradation of flavor quantified in terms of piperine and oleoresin content in pepper powder

In order to arrive at kinetic data, a first order degradation was presumed. Accordingly, '$\ln(C/C_0)$' was plotted vs time '*t*' (s), from

Table 1
Effect of heat treatment on piperine and oleoresin content[a,b,c] of black pepper powder.

Temperature (°C)	Time (min)	Piperine (%)	Oleoresin (%)	Temperature (°C)	Time (min)	Piperine (%)	Oleoresin (%)
50	0	3.520	10.400	90	0	3.52	10.400
	20	3.514	10.406		20	3.442	8.428
	40	3.488	10.399		40	3.383	6.844
	60	3.490	10.402		60	3.331	5.992
60	20	3.520	10.335	100	20	3.429	6.452
	40	3.486	9.565		40	3.348	5.314
	60	3.474	8.765		60	3.246	4.263
70	20	3.502	10.247	110	20	3.369	6.480
	40	3.474	9.490		40	3.219	4.519
	60	3.456	8.430		60	2.991	3.689
80	20	3.468	9.792	120	20	3.154	5.990
	40	3.437	8.495		40	2.700	4.080
	60	3.400	7.893		60	2.300	2.700

[a] Values given as % of black pepper.
[b] All the readings are average of three or more values.
[c] The standard error values were less than 0.004.

Table 2
Rate constant k[a,b] and correlation coefficient (R^2) for flavour degradation in black pepper powder.

Temperature (°C)	Piperine			Oleoresin		
	k (min^{-1})	R^2	$T_{1/2}$ (min)	k (min^{-1})	R^2	$T_{1/2}$ (min)
50	–	–	–			
60	–	–	–	0.0041	0.99	169
70	0.0003	0.99	2310	0.0049	0.99	141
80	0.0005	0.99	1386	0.0059	0.97	117
90	0.0008	0.99	866	0.0085	0.98	82
100	0.0014	0.99	495	0.0104	0.99	67
110	0.0030	0.98	231	0.0141	0.98	49
120	0.0076	0.99	91	0.0199	0.99	35

[a] Calculated from semi-log plot of Ln (C_t/C_0) vs time.
[b] The standard error in k values were less than.

which rate constant, 'k' was calculated as the slope. A correlation coefficient > 0.9 in all cases confirmed that the degradation of piperine and volatile oil to follow first order reaction kinetics. Figs. 1 and 2 show the representative plots for piperine at 80, 100 and 110 °C and volatile oil loss at 80, 100 and 120 °C, respectively. The time required for piperine and oleoresin to degrade to 50% of its original value was calculated from the rate constant as '$0.693/k$'.

Table 2 documents the rate constants and '$t_{1/2}$' (min) for piperine and volatile oil. The rate constants for piperine increased from 0.0003/min at 50 °C to 0.0074/min at 120 °C with a corresponding decrease in half-life from 2310 min to 91 min. Rate constants for volatile oil loss varied from 0.0041/min at 50 °C to 0.0199/min at 120°. It can be seen that the degradation is faster for volatile oil as compared to piperine at all temperatures.

Fig. 3 shows the Arrhenius plot for piperine degradation and oleoresin loss in pepper powder. The linear nature of the plots obtained indicate thermal destruction of flavor (piperine and oleoresin) to conform to Arrhenius equation. Activation energies E_a, (J mol^{-1}) were calculated as a product of gas constant, R (8.3145 J mol^{-1} K^{-1}) and the slope of the graph obtained by plotting '$\ln k$' vs '$1/T$'. The activation energy of piperine degradation and oleoresin loss in pepper powder was found to be 66.8 kJ mol^{-1} and 27.14 kJ mol^{-1}. It can be observed from the activation energies that piperine is comparatively stable at lower temperatures and is more sensitive to higher temperatures as indicated by higher activation energy.

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

To extend the results obtained from isothermal experiments to the non-isothermal encountered in the three modes of cooking, viz. open pan cooking, pressure cooking and cooking in 'EcoCooker', time–temperature data during the processing of each was recorded (Fig. 4).

3.4. Degradation profile of flavor in pepper powder under the three modes of cooking

Flavor degradation was followed in each of these modes of cooking as for pepper powder under isothermal conditions. The results documented in Table 3 indicate that degradation was maximum in pressure cooking, may be due to higher cooking temperature, though the magnitude of difference in the degradation is not so significant as compared to other cooking methods. The degradation of piperine in open pan, pressure cooking and in EcoCooker were 5%, 12.5% and 6%, respectively and the corresponding decrease in oleoresin content were 24%, 22% and 29%. Suresh et al. (2007) reported that maximum piperine loss is observed during pressure cooking (34%) as compared to boiling (27%). A degradation of 13–17% reported when black pepper powder was used as a spice ingredient in *rasam* making (Srinivasan et al., 1992).

3.5. Prediction of flavor (piperine and oleoresin) loss during non-isothermal heating processing

To predict the degradation occurring during a given non-isothermal heating process, the Arrhenius equation (Eq. (3)) was used. The rate constant 'k_T' at each temperature was calculated using Eq. (3) substituting for 'T' from the time temperature data of non-isothermal heating process. Knowing the rate constant k_T, the rate (dC/dt), amount degraded (ΔC) during the short time interval zero to t (Δt_T) during non-isothermal process and the final flavor '$C_{t+\Delta t}$' can be calculated as follows.

Rate, $dC/dt = k_T \times C_t$, where C_t is the concentration at time 't'

$$(\Delta C) = \text{Rate} \times t_T(k_T \times C_t \times t_T)$$

$C_T = C_t - \sum_{i=0}^{i=n} \Delta C$, where C_T is the concentration after time 't'.

These calculations were continued for the entire time period (heating and constant temperatures) at which each cooking process was done. An MS excel based computer program was used to calculate the above parameters.The total amount degraded after complete cooking = $\sum\Delta C$.The final quantity thus will be $C_0 - \sum\Delta C$, where C_0 is the initial Concentration.

The resulting predictions and the actual degradation, obtained experimentally, are given in Table 4. As seen, a reasonably good agreement between the actual and the predicted degradation/retention of flavor (piperine & oleoresin) was obtained. Using this prediction method, the degradation of can be predicted for any heat processing method, if the time–temperature profile of that heat processing operation is known.

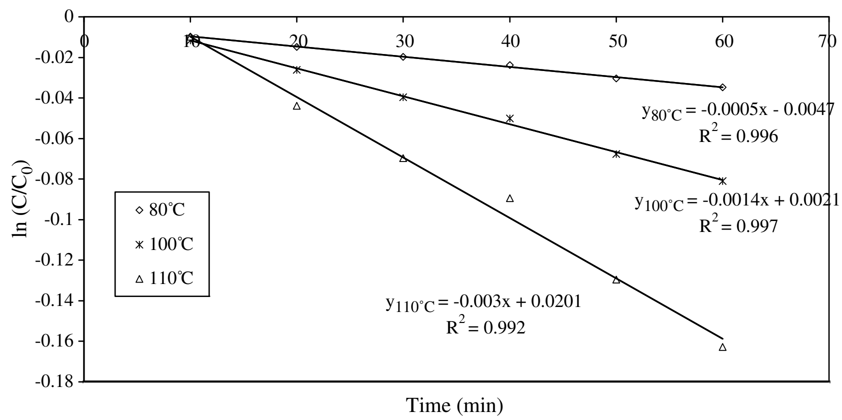

Fig. 1. First order plots for piperine degradation at 80, 100 and 110 °C.

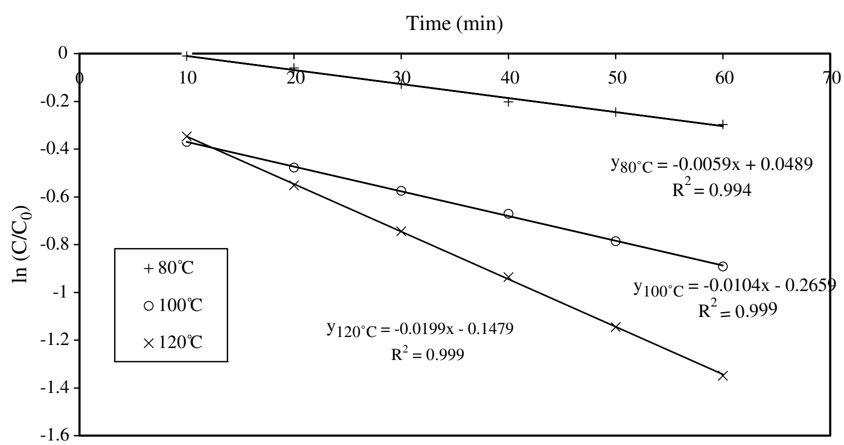

Fig. 2. First order plots for oleoresin loss at 80, 100 and 120 °C.

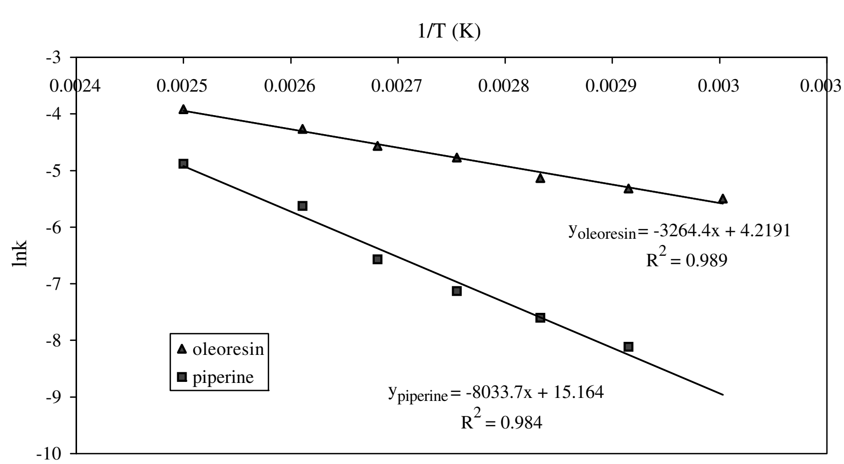

Fig. 3. Arrhenius plots for piperine degradation and oleoresin loss.

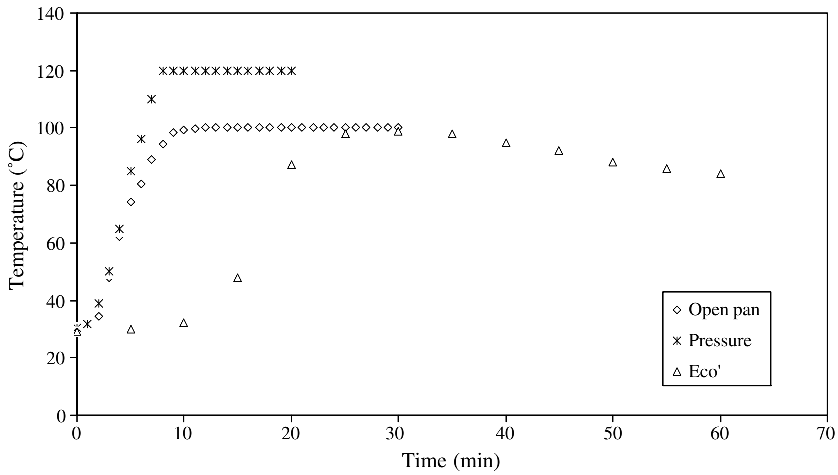

Fig. 4. Time–Temperature profiles of different cooking methods used.

Table 3
Degradation profile, rate constant k, half-life ($T_{1/2}$) and correlation coefficient (R^2) of flavour profiles (piperine and oleoresin) of black pepper powder at different cooking methods.

Cooking method	Time (min)	Piperine (%)	k (min^{-1}) (R^2)[a]	$T_{1/2}$ (min)	Oleoresin (%)	k (min^{-1}) (R^2)[a]	$T_{1/2}$ (min)
Open pan	0	3.52	0.0053 (0.981)	130	10.400	0.0134 (0.971)	52
	10	3.478			10.310		
	20	3.438			9.389		
	30	3.372			7.890		
Pressure	10	3.44	0.0162 (0.992)	43	10.371	0.025 (0.998)	28
	15	3.376			9.229		
	20	3.082			8.075		
EcoCooker[b]	10	3.501	0.009 (0.996)	77	10.286	0.020 (0.989)	35
	20	3.42			8.120		
	30	3.321			6.890		

The standard error values were less than 0.05.
[a] Correlation coefficient.
[b] Held for 30 min as per the protocol recommended for cooking with 'EcoCooker'.

Table 4
The actual and predicted degradation of flavour profile[a] of black pepper powder in different cooking methods.

Cooking method	Piperine		Oleoresin	
	Actual degradation	Predicted degradation	Actual degradation	Predicted degradation
Open pan	3.372	3.356	7.89	7.78
Pressure	3.082	3.090	8.07	8.01
EcoCooker[b]	3.321	3.300	7.29	6.52

[a] Values given as % of black pepper.
[b] Held for 30 min as per the protocol recommended for cooking with 'EcoCooker'.

4. Conclusions

The loss of flavor evaluated in terms of piperine and oleoresin content found to follow first order kinetics. Fuel-efficient 'EcoCooker' shows no significant difference in the magnitude of retention of flavor as compared to normal open pan and pressure cooking methods. Since the spices are valued for their unique flavor profiles, it is important to know the kinetics of flavor loss for each of the spices. Therefore the needs to study the kinetics of flavor loss for other spices are also warranted.

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