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Generation of Shelf Life Equations of Cauliflower

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Abstract

Pre-harvest quality of Cauliflower depends upon growing climate and is also affected by the particular cultivar (PUSA Katki, Giant Snow Ball, Himani etc.), soil type, production system (Conventional, Organic).But post-harvest treatment largely determines final quality, whether a crop is sold for fresh consumption, or used as an ingredient in a processed food. Each crop has an optimum range for storage temperature and humidity on which its shelf life depends. To develop the shelf life equations of Cauliflower various intrinsic and extrinsic vegetable parameters are studied. Relationship between these parameters is used to develop generalized mathematical equation of Shelf Life of Cauliflower in terms of important of Cold Storage operating parameters namely Temperature and Relative Humidity. To solve this generalized mathematical equation, Arrhenius reaction kinematics approach is used to generate shelf life equations in terms of three important quality parameters of Cauliflower namely Moisture Loss, Energy Value and Vitamin C. Changes in these quality parameters w.r.to variation in Temperature and Relative Humidity are measured with standard procedures in laboratory . Then by fixing kinematics reaction order and differential rate laws, shelf life equations for Cauliflower are developed. Laboratory measured values are compared with calculated values obtained from shelf life equations. These equations are useful to retain the Cauliflower quality and its nutritional value in post-harvest management. These equations will definitely provide fundamental platform to design and develop cost effective cold storages for Vegetable Preservation in India.

Keywords: Cruciferous; intrinsic; extrinsic; sensory/organoleptic; chemical reaction kinematics

1. Introduction

In the global endeavor for food and nutritional security, the vegetable crops and their nutritional value are of special significance. In addition, vegetables are usually higher in productivity, have shorter maturity cycle, high value and provide a valuable source of income, leading to improved livelihood. Vegetables can contribute largely to solve the food and nutritional problems of the country. In India, demand of vegetables will be 170 million tonnes by 2025, whereas the expected production at the present growth rate would be about 160 million tonnes. [1]

Fruits and vegetables are the most perishable agricultural produces and the post-harvest losses of these are tremendous. Environmental factors that influence the post-harvest losses in fruits and vegetables are temperature, humidity, composition and proportion of gases in controlled atmospheric storage etc. Inadequate harvesting, transportation and handling, storage and marketing facilities and legislation lead to the conditions favourable for secondary causes of loss. Cauliflower comes under most perishable commodity type vegetable category and 90% of its consumption is in fresh condition only. Aim of this paper is to develop and promote science based information and technology that will lead to increase in the consumption of cauliflower by enhancing its post-harvest quality by establishing appropriate integrated cold chain. [2]

To accomplish this aim through

1) Define sensory parameters that describe consumer perception e.g. Cauliflower quality,
2) Correlate sensory parameters with objective measurable quality parameters such as moisture content, Energy Value, Vitamin C etc.
3) Identify optimal post-harvest and processing parameters that maximize quality and nutritional value of Cauliflower. [3]

Shelf life: is the time frame over which a food product can be relied upon to retain its quality characteristics. Shelf life encompasses several facets of food quality including safety, nutritional value, and sensory properties. Shelf life affects food quality, which in turn influences the consumer's buying decisions. [4]

Shelf life determination: can be done either with or without specialized equipment. There are two methods of shelf life determination. Direct method involves storing the product under preselected conditions for a period of time longer than the expected shelf life and checking the product at regular intervals to see when it begins to spoil. The exact procedure is unique for each product.

Indirect method approach uses accelerated storage and/or predictive microbiological modelling to determine a shelf life.[5]

2. Quality Parameters of Cauliflower

A. Intrinsic Parameters

Intrinsic parameters are those factors that are an integral part of a foods physical makeup, including water activity, pH, moisture content, and anti-microbial agents etc.

Shrinkage of nearly all food commodities is a factor to be considered in cold-storage handling. Cauliflowers lose weight during cold storage. Cauliflower, being a living organism, undergoes metabolic changes as a result of vital intrinsic parameters. The most important means of weight loss or moisture loss are evaporation, respiration and decrease in water activity.

Loss in weight caused by a decrease in moisture content of vegetables as a result of evaporation while in transit or storage is sometimes referred to as desiccation. Evaporation is reverse action of condensation, both of which occur because of vapour-pressure differentials.

The agents, which influence the extent of weight loss are: stage of the maturity at the time of harvest; quality of cauliflower florets as well as injury during harvesting and storing; storage temperature and relative humidity during a short time after harvesting; temperature, humidity and amount of ventilation during storage and length of storage. The loss in weight is directly proportional to the temperature and period of storage. [6, 7]

B. Intrinsic Parameters of Cauliflower (mathematical notation 'u')

1) Physical: (mathematical notation 'y_1')

TABLE I
PHYSICAL W.R.T SHELF LIFE

Sr No	Physical Parameter	Relationship with Shelf Life
1	Moisture Loss	$\propto \theta_s$
2	Firmness	$\propto \theta_s$
3	Weight	$\propto \theta_s$

2) Chemical/Enzymatic: (mathematical notation 'y_2')

TABLE II
MICROBIOLOGICAL W.R.T SHELF LIFE

Sr No	Microbiological	Relationship with Shelf Life
1	Mesophilic Aerobes Count	$\propto \theta_s$
2	Yeast and Mould	$\propto 1/\theta_s$
3	Coliform Bacteria/E. Coli	$\propto 1/\theta_s$

3) Microbiological :(mathematical notation 'y_3')

TABLE III
CHEMICAL W.R.T SHELF LIFE

Sr No	Chemical/Enzymatic	Relationship with Shelf Life
1	Water Activity a_w	$\propto 1/\theta_s$
2	Respiration Rate	$\propto 1/\theta_s$
3	PH	$\propto 1/\theta_s$
4	Rancidity	$\propto \theta_s$
5	Energy Value	$\propto \theta_s$
6	Vit C	$\propto \theta_s$

4) Organoleptic/Sensory: (mathematical notation 'y_4')

TABLE IV
ORGANOLEPTIC W.R.T SHELF LIFE

Sr No	Organoleptic/Sensory Parameters	Relationship with Shelf Life
1	Appearance	$\propto \theta_s$
2	Colour	$\propto \theta_s$
3	Taste	$\propto \theta_s$
4	Odour/Smell	$\propto \theta_s$
5	Texture	$\propto \theta_s$
6	Presence of Larvae	$\propto 1/\theta_s$

C. Extrinsic Parameters

Extrinsic parameters are those factors that can be controlled or changed to influence a product's shelf life, including temperature, time, relative humidity, presence of gases, and other environmental factors. [5]

Temperature is the single most important factor in maintaining quality after harvest. Higher the storage temperature less will be the shelf life of any vegetable.

Refrigerated storage retards the following elements of deterioration in perishable crops:

1) aging due to ripening, softening, and textural and color changes;
2) undesirable metabolic changes and respiratory heat production;
3) moisture loss and the wilting that results;
4) spoilage due to invasion by bacteria, fungi and yeasts

Relative Humidity is directly proportional to shelf life of vegetable. If air is dry, moisture will be taken from the foods being stored, causing wilting in vegetables. If the air is too moist, the foods will decay, especially if temperatures vary. [7, 8, 19]

1) Extrinsic Parameters of Cauliflower: (mathematical notation 'v')

Table V: Extrinsic Parameters w.r.t Shelf Life

Sr No	Parameters	Relationship with Shelf Life
1	Temperature*	$\propto 1/\theta_s$
2	RH*	$\propto \theta_s$
3	O_2	$\propto \theta_s$
4	CO_2	$\propto \theta_s$
5	Air Velocity	$\propto 1/\theta_s$
6	Solar Radiation	$\propto \theta_s$
7	Mechanical Handling	$\propto 1/\theta_s$
8	Atmospheric Pressure	$\propto 1/\theta_s$
9	Cooling Rate	$\propto \theta_s$
10	Cooling Equipment	$\propto \theta_s$

3. Generalized Mathematical Equation For Shelf Life Of Cauliflower

$$\theta_s = f\ (u, v) \tag{1}$$

Where u = Intrinsic Parameters
v = Extrinsic Parameters

$$\begin{aligned}\theta_s &= f\ (u, v) \\ &= f\ (y_1, y_2, y_3, y_4, v) \\ &= f\ (x_1, x_2, x_3 \ldots x_n, z_1, z_2, z_3 \ldots\ldots z_{10}) \\ &= f\ (z_1, z_2, z_3 \ldots\ldots z_{10})\end{aligned}$$

Where y_1 = Physical Intrinsic Parameters
y_2 = Chemical Intrinsic Parameters
y_3 = Microbiological Intrinsic Parameters
y_4 = Organoleptic Intrinsic Parameters
$x_1, x_2, x_3 \ldots x_n$ = Cauliflower Property Intrinsic Parameters
$z_1, z_2, z_3 \ldots z_{10}$ = Storage Extrinsic Parameters

But, important governing storage parameters* are Temperature (t) and Relative Humidity of air (RH).

$$\frac{\partial \theta s}{\partial t} = \sum_{j=1}^{4} \sum_{i=1}^{n} \left(\frac{\partial \theta s}{\partial u}\right) \cdot \left(\frac{\partial u}{\partial yj}\right) \cdot \left(\frac{\partial yj}{\partial xi}\right) \cdot \left(\frac{\partial xi}{\partial t}\right) + \frac{\partial \theta s}{\partial v} \cdot \frac{\partial v}{\partial t} \tag{2}$$

$$\frac{\partial\theta s}{\partial RH} = \sum_{j=1}^{4} \sum_{i=1}^{n} \left(\frac{\partial\theta s}{\partial u}\right) \cdot \left(\frac{\partial u}{\partial yj}\right) \cdot \left(\frac{\partial yj}{\partial xi}\right) \cdot \left(\frac{\partial xi}{\partial RH}\right) + \frac{\partial\theta s}{\partial v} \cdot \frac{\partial v}{\partial RH} \quad \textbf{(3)}$$

To represent equations (2) and (3) in Matrix form and to get shelf life with respect to variation in Temperature and Relative Humidity will be a huge mathematical task.

Hence, one useful approach to quantifying the effect of temperature on food quality is to construct shelf life plots (Labuza and Kamman, 1983). The two most-used models are the Arrhenius and Linear. These models are used to represent the relationship between the rate of a reaction (or the reciprocal of rate which can be time for a specified loss in quality or shelf life) and temperature.
The equations for these two models are

$$\theta_s = \theta_o \exp \frac{E_A}{R}\left[\frac{1}{T_s} - \frac{1}{T_o}\right] \quad \textbf{(4)}$$

And

$$\theta_s = \theta_o \, e^{-b(T_s - T_o)} \quad \textbf{(5)}$$

Where θ_s = shelf life at temperature T_s and θ_o = shelf life at temperature T_o.

If only a small temperature range is used (less than $\pm$4°C), there is little error in using the linear plot rather than the Arrhenius plot. In the generation of shelf life equations of Cauliflower Arrhenius model approach is used. (Rosenfeld, 1984) [9, 10]

4. Kinetics of Shelf life Testing and Measurement

The prediction of shelf life for food products is based on the application of the principles of temperature dependent chemical reaction kinetics. These reaction rates depend on product composition as well as environmental factors, i.e., temperature, humidity, atmosphere, etc. Basic to any predictive use of reaction kinetics is that the relationship between the measurable changing reaction parameter and time be linear. Labuza3 has reported that quality loss follows the equation

$$dA/dt = k(A)^n \quad (6)$$

Where dA/dt is the change in the measurable quality factor A with time, k is the rate constant in appropriate units, and n is the order of the chemical reaction of the quality factor. The order of reaction for most quality attributes in food products is either zero, first or second. [10]

Effect of temperature on reaction rates:

The Arrhenius relationship is often used to describe the temperature dependence of deterioration rate.

$$k = ko \exp(-Ea/RT) \tag{7}$$
$$\text{Or } \ln k = \ln ko - Ea/(RT) \tag{8}$$

Where ko is a pre-exponential factor; Ea is an activation energy for the reaction in J mol^{-1}; R is the gas constant = 8.31 J K^{-1} mol^{-1}; T is an absolute temperature in K (273 + °C).When the temperature increases, the rate of a reaction increases too because the rate constant increases. [9]

The rate constant k is only a constant for a particular temperature. Changing the temperature changes the value of k because the proportion of constituents that have the required energy (greater than the activation energy) is increased. [9, 12]

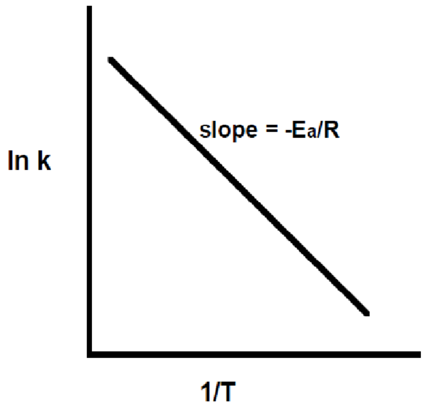

Fig. 1 Variation of activation energy w.r.to Temperature and rate constant

Fig. 1 shows that a plot of lnk against 1/T gave a straight line whose gradient is $-E_A/R$ is called as Arrhenius Plot. [9, 12]

5. Shelf Life Equation of Cauliflower based on Moisture Loss

Water loss in fresh vegetables results in a wilted, dull appearance that reduces eye appeal and freshness. Preventing water loss improves shelf life, appearance and desirability.

Water activity, a_w, is a physical property that has a direct implication for microbiological safety of food.

$$a_w = ERH/100 \tag{9}$$

ERH = Equivalent Relative Humidity (By definition a_w is 1 for Pure Water) or

$$a_w = P/Po = \%RH/100 \tag{10}$$

Where, p = vapor pressure of water in food, Po = partial pressure of water at same temp.

a_w of Cauliflower = 0.98

The ERH of a food product is defined as that relative humidity of the air surrounding the food at which the product neither gains nor loses its natural moisture; that is, it is in equilibrium with its environment. At a relative humidity above the ERH, the product will gain moisture and at humidity below that level, it will lose moisture. A food with a_w of 0.6 will lose moisture at a relative humidity below 60% and gain moisture above 60%. [15, 18]

In zero order reactions, the rate of loss of the quality factor is constant or linear and the resulting curve will be linear on a linear plot. If the gradient is constant, showing that the rate is unaffected by the concentration of a reactant, it is a zero order reaction for that reactant.

$$Ao - Ae = kz\theta s \tag{11}$$

$$\theta s = (Ao - Ae)/kz \tag{12}$$

Where Ao= Initial Moisture Content, Ae= Final Moisture content at accepted θs,
θs= Measured and sensory acceptable Shelf Life, kz = rate of loss in moisture content

Moisture loss is a physical change in Cauliflower. It predominantly depends on storage conditions. Hence, zero order differential law is used to quantify moisture loss. [9, 10, 11]

Table VI: Variation of Moisture Loss, Rate Constant Kz With Respect To Shelf Life Cauliflower (Measured And Calculated Values)

C. S Temp ˚C	**T..K**	**RH %**	**Measured θs in Days**	**kz=(Ao-Ae) /θs**	**Ao-Ae**	**1/T**	**lnkz**
0	273	90	30	0.022	0.66	0.003663	-3.816713
5	278	80	25	0.0424	1.06	0.003597	-3.160607
10	283	70	20	0.073	1.46	0.003534	-2.617296
15	288	60	15	0.124	1.86	0.003472	-2.087474
20	293	50	12	0.188333333	2.26	0.003413	-1.669542
25	298	40	9	0.295555556	2.66	0.003356	-1.218898
30	303	35	6	0.51	3.06	0.0033	-0.673345
35	308	30	3	1.153333333	3.46	0.003247	0.1426563
40	313	20	1	3.86	3.86	0.003195	1.3506672

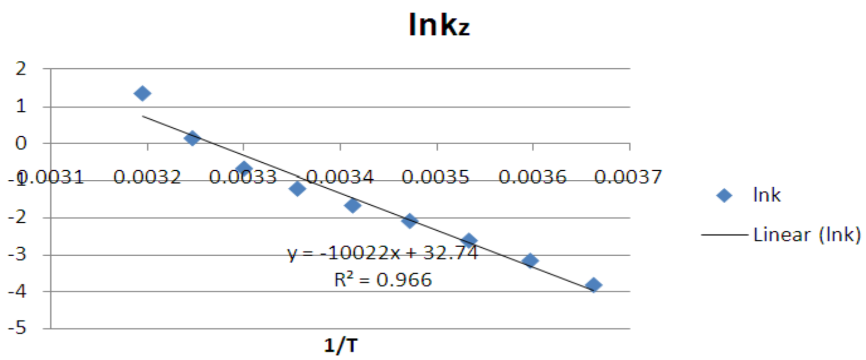

Fig.2 Variation of lnk with respect to absolute temperature

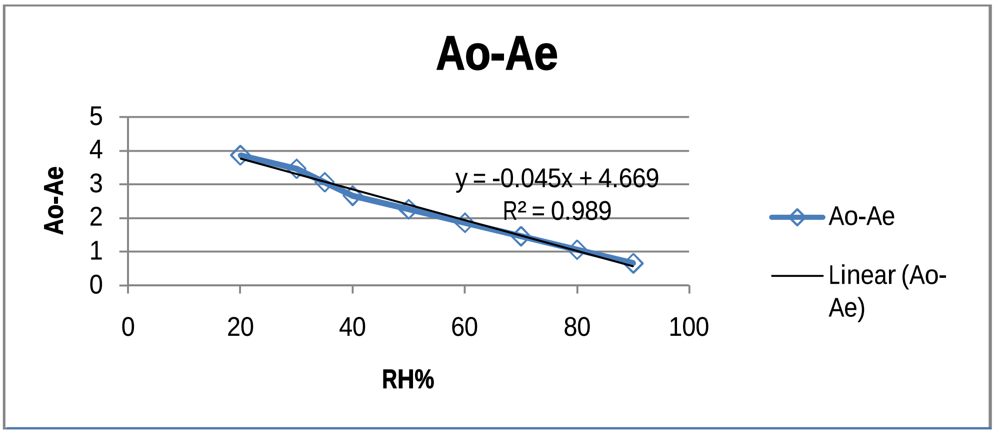

Fig.3 Relationship of moisture loss with respect to RH

Table VII: Initial Conditions of Cauliflower

Temp °c	RH %	Moisture g/100g(Ao)	Shelf Life.. Days
30	40	90.22	0 (Fresh Cauliflower)

Table VIII : Calculated Shelf Life of Cauliflower at given T and RH

Temp in ˚C	T in k	RH%	Measured θs in days	Ae (g/100g)	Calculated θs1= (-0.045*RH+4.669) /exp ((-10022*1/T)+ 32.74) in Days
0	273	90	30	89.56	33
5	278	80	25	89.16	29
10	283	70	20	88.76	22
15	288	60	15	88.36	15
20	293	50	12	87.96	10
25	298	40	9	87.56	7
30	303	35	6	87.16	4
35	308	30	3	86.76	3
40	313	20	1	86.36	2

Therefore, Shelf Life Equation of Cauliflower based on Moisture Property is

$$\theta s_1 = \frac{-0.045*RH+4.669}{e^{[\left(-10022*\frac{1}{T}\right)+32.74]}} \quad (13)$$

6. Shelf Life Equation of Cauliflower based on Energy Value Property

First order reactions are not linear but are dependent on the amount of the quality factor that remains in the cauliflower at the time. If the gradient changes exponentially, it is a **first order reaction**. In these types of reactions, a linear prediction curve is constructed using semi logarithmic coordinates.

Typical first order reactions are: (1) rancidity, (2) microbial growth and death, (3) energy value products, and (4) loss of protein quality.

$$[A]_e = [A]_o \cdot e^{-k_f \theta_s} \quad (14)$$

$$\theta_s = \frac{ln \frac{[A]o}{[A]e}}{kf} \quad (15)$$

Where A_o= Initial Energy Value, A_e= Measured Energy Value at accepted θ_s,

θ_s= Measured and sensory acceptable Shelf Life, k_f = rate of increase in energy value[9,10,11]

Table IX: Initial Conditions of Cauliflower

Temp °c	RH %	Initial Energy Value (Ao) kcal/100g	Shelf Life... Days
30	40	90.22	0 (Fresh Cauliflower)

Table X: Calculated Shelf Life of Cauliflower at given T and RH

Temp ˚C	T..... K	RH%	Measured θs in Days	Ae kcal/100g	Calculated θs2= (-0.002*RH+0.363)/exp((-7410*1/T)+ 21.66) in Days
0	273	90	30	45.2	44
5	278	80	25	45	30
10	283	70	20	46.5	21
15	288	60	15	47	14
20	293	50	12	48	10
25	298	40	9	49	7
30	303	35	6	54	5
35	308	30	3	58	3
40	313	20	1	62	2

Therefore, Shelf Life Equation of Cauliflower based on Energy Value is

$$\theta s_2 = \frac{-0.0043*RH+0.4563}{e^{[(-9315*\frac{1}{T})+28.06]}} \quad (16)$$

7. Shelf Life Equation of Cauliflower based on Vitamin C Property

If the gradient changes from very high at t = 0 and then slows down, it is a **second order reaction**. The loss of vitamin C in liquid preparations has been called a second order reaction because it is dependent on the level of both the ascorbic acid and oxygen. Reciprocal plots are linear for these reactions. [7, 8, 10]

$$1 / [A]_e = 1 / [A]_o + k_s\theta_s \qquad (17)$$

$$\theta_s = 1/[A]e - 1 / [A]o /ks \qquad (18)$$

Where A_o= Initial Vitamin 'C' Value, A_e= Measured Vitamin Value at accepted $\theta_{s,}$

θ_s= Measured and sensory acceptable Shelf Life, k_s = rate of increase in energy value[9,10,11]

Table XI: Initial conditions of Cauliflower

Temp °c	RH %	Initial Vitamin C (A_o) mg/100g	θ_s.. Days
30	40	40mg/100g	0 (Fresh Cauliflower)

Table XII: Calculated Shelf Life of Cauliflower at given T and RH

Temp in ˚C	T.. k	RH%	Measured θs in Days	Ae mg/100g	Calculated θs3= (0.074*RH-0.574)/100/exp((-1874*1/T)+ 0.595) in Days
0	273	90	30	12.5	32
5	278	80	25	13.2	25
10	283	70	20	13.9	19
15	288	60	15	14.7	14
20	293	50	12	15.2	10
25	298	40	9	16.4	7
30	303	35	6	23.6	5
35	308	30	3	32.2	4
40	313	20	1	33.8	2

Therefore, Shelf Life Equation of Cauliflower based on Vitamin C is

$$\theta s_3 = \frac{(0.074 * RH - 0.574)/100}{e^{[(-1874 * \frac{1}{T}) + 0.595]}} \qquad (19)$$

8. Conclusion

Shelf life equations of cauliflower are the unique application of the Arrhenius equation synthesized with laboratory measured values of Intrinsic and Extrinsic parameters. These equations will form the basis of Cold Storage designs for

Vegetables. The causes of cauliflower deterioration are predominantly temperature and relative humidity related. Research supports the common perception that fresh is often best for optimal nutritive content, as long as the fresh product undergoes minimal changes during storage at either room or refrigerated temperatures. [16, 18]

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