Kinetic Modeling of Quality Change in Ethiopian Kent Mango Stored Under Different Temperature

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Abstract. Model simulations permit to identify and predict the levels of loss arising under different storage temperature and maturity conditions in the supply chain. In this research kinetic model was developed for predicting relationship between storage temperature and mango quality attributes. Three quality attributes of mango (color, firmness and total soluble solids (TSS)) were measured and used for the kinetic modeling by estimating the parameters of the model. Mangoes were stored at 7, 13 °C and room temperature. The measurements were carried out with eight repetitions at one week intervals. From the tested equations exponential model for color and TSS found to be the best fit and logistic model for firmness. The model parameters were estimated by the simulation and also validated with a separate experiment with acceptable standard errors and minimum confidence interval of 87.58% which means that the variation in the measured data could be explained by the model. After developing the model a ripening stage were assigned from 1 to 5 with the corresponding quality values; where 1 is the mature green and 5 is the over ripe stage. The result shows that softening was the limiting quality factor for mangoes stored at 7 °C and color was the limiting quality factor for mangoes stored at 13 °C and room temperature. Equations used in this research could be used to estimate quality loss at different conditions of mango fruit in the supply chain.

Keywords: Mango · Quality · Kinetic modeling · Firmness · Color · Total soluble solids · Temperature

1 Introduction

Consumers and retailers prefer good quality fresh fruits in the market and through the supply chain. Quality changes, including physiological, microbiological, and physical and biochemical happen during postharvest cold storage [1]. These changes are mainly

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depending on temperature because temperature of the fruit affects respiration rate, shelf-life and quality deterioration during storage period [9]. Therefore, it is important to have tools to control, and to predict the quality of fruit stored under different temperatures [7]. Mathematical modeling can help to gain insight in the mechanisms underlying postharvest losses and quality changes by screening hypothetical conceptual models on their fitness to explain the data. Model simulations permit to identify and predict the risk and levels of quality change [1] and waste arising under different ambient variables, processing conditions and logistic scenarios.

To understand the postharvest physiological behavior of fresh produce knowledge of the physiological, biochemical processes, and their relations are critical [8]. Physical, chemical, and biochemical factors are internal factors, however external factors like temperature in the fruit supply chain also affect fruit quality and can be modeled [11]. The focus of this study was to develop models describing the evolution of specific quality attributes (firmness, color and (TTS) total soluble solids) as a function of temperature. Firmness and color are the most important quality parameters used by consumers and retailers to determine the quality of mango and TTS is usually used in research and commercial farms [12]. These phenomena were modeled with mechanistic models that are based on physiological phenomena taking place in the fruit. These equations are solved numerically. The model parameters were estimated and validated based on experiments with Ethiopian Kent mango fruit stored under different temperature conditions in the refrigerated units.

2 Materials and Methods

2.1 Experimental Study

Mango fruits were obtained from a Horizon commercial farm through Etfruit (Ethiopian Fruit marketing agency). Normally the export standard mangos in Ethiopia are from Tommy Atkins, Keitt and Kent cultivars which are being cultivated by the commercial farms. One of the main reasons for the drop in mango exports from Ethiopia has been the variable and low quality of mango on arrival in overseas countries [9]. The experimental work was conducted with the cultivar Kent because of its longer shelf life and importance for the export market. Kent is quite similar looking cultivar with Keitt but Kent matures earlier March in Ethiopia [10]. Harvesting was carried out manually at commercial maturity. Plastic containers were used for transporting the fruits to the storage facility at the chemical and bio engineering, analytical laboratory of Addis Ababa institute of technology, immediately after harvest. Fruits were selected for weight in the range of 200–300 g. The mangoes were washed with tap water to remove field heat, soil particles, and to reduce microbial populations on the surface.

Mangoes were stored at 7, and 13 °C and at room temperature (25 °C) for experiment periods up to 21 days. 7 °C was selected to check the occurrence of chilling and quality change with other temperatures because some mango cultivars can safely be stored at 7–8 °C for up to 25 days [13]. Analyses were done for firmness, color, total soluble solid (TTS) content, total titratable acidity and weight loss but only three parameters were discussed in this study. Firmness was measured using a hand held FT-10 fruit tester penetrometer with a reading range of 5 kgf to 50 kgf with accuracy of ±0.5 and a cylindrical plunger with surface area of 1 cm^2 at the tip. First the outer skin from both cheeks was peeled from each fruit to reduce the effect of the hard skin and then the force applied per area of the inner fruit flesh is measured to a depth of 8 mm. Two measurements were taken on the equator for each mango fruit flesh after peeling the skin and the average was taken as the firmness.

Color change of mango fruit was measured by using a standard color chart used for Kent cultivar. For this cultivar due to pigment accumulation, flesh color change from 1-deep green, 2-light yellow-green, 3-yellow-light green, 4-yellow-orange and 5-golden orange during the ripening period [8]. The color was measured at the cheeks of the fruit near the two equators and the average was calculated for each fruit. TTS was measured by using a bench-top 60/70 ABBE refractometer, with a reading range of 0–32° Brix with accuracy of ±1. The mango peal was cut off and a few drops of juice squeezed by hand directly onto the sensor of a digital refractometer and read the °brix from the measuring device and the average value is taken from two measurement of a mango fruit around the cheeks.

2.2 Modeling and Simulations

Kinetic model was developed for predicting relationship between storage and shelf life conditions and mango quality attributes. Three quality attributes of mango (colour, firmness and total soluble solids) were selected for the kinetic modelling from the measured parameters. These selected parameters are the most important quality parameters used by consumers and retailers to determine the quality of mango. Moreover, they are traditionally used for grading and fixing the price of mango fruits in the Ethiopian supply chain [2]. The quality model was then simulated using OpitiPa software which is used to model and validate ordinary differential equations based simulation models in the area of food and postharvest [6].

Firmness Change Modeling. Fruit softening is correlated to the amount of pectin being cleaved [7] and converted to Galacturonic acid and demethylated pectin by pectic enzymes [5]. Simplified equation of the reaction is

$$P + E_{pect} \overset{k_{pect}}{\rightarrow} G + E_{pect} \tag{1}$$

where P is the amount of pectin; E_{pect} is the amount of the pectic enzyme; and k_{pect} is the rate of conversion of pectin to Galacturonic acid (G).

The amounts of pectic enzymes in fruit are generally governed by two reactions, one for formation and the other for denaturation [1]. The model was developed describing the activity of pectin enzyme during storage [5]. It was assumed that an inactive precursor (E_{pre}) that is activated into the active form of pectin enzyme (E_{pect}) that subsequently can be denatured again (E_{den}) [1].

$$E_{pre} + E_{pect} \overset{k_e}{\rightarrow} 2E_{pect} \tag{2}$$

$$E_{pect} \overset{k_{E_{den}}}{\rightarrow} E_{den} \tag{3}$$

where E_{pre} is the precursor of the pectic enzyme; k_e is the rate of formation of pectic enzyme; k_{Eden} is the rate of denaturation of pectic enzyme; E_{den} is the denatured enzyme and E_{pect} is the pectic enzyme.

The following equations of chemical kinetics assuming first order reactions can be derived:

$$\frac{d[P]}{dt} = -k_{pect}[P][E_{pect}] \tag{4}$$

$$\frac{d[E_{pect}]}{dt} = 2 * k_e[E_{pre}][E_{pect}] - k_{E_{den}}[E_{pect}] \tag{5}$$

$$\frac{d[E_{pre}]}{dt} = -k_e[E_{pre}][E_{pect}] \tag{6}$$

For modeling the firmness change of mango during storage period autocatalytic enzyme reaction, Michaelis-Menten enzyme kinetics and exponential models were tested for their accuracy in determining the change of firmness at 7, 13 °C and room temperature. From the tested equations exponential model shows the best fit and also happen to be less complex than autocatalytic enzyme reaction and Michaelis-Menten enzyme kinetics equations.

Color of Mango Fruit. Color changes in mango fruit are due to the disappearance of chlorophyll and appearance of other pigments [6]. Chloroplasts are transformed to chromoplasts containing yellow or red pigments [9]. These are two parallel pathways, the net reaction is assumed to be autocatalytic in a sense that the process is catalyzed by an enzyme that itself is being promoted as a result of the underlying ripening process. For this study, the whole process was simplified into one simple reaction:

$$P_1 + E_C \overset{k_C}{\rightarrow} P_2 + 2E_C \tag{7}$$

where P_1 refers to one pigment complex (chlorophyll) that is being converted into another pigment complex P_2 (lycopene) while E_C is doubled.

Three different reaction rate kinetic models (zero-order, first order and logistic model) were tested in this study and first order exponential model was selected for the simulation by considering the model complexity and model applicability, while respecting literature knowledge on color change as explained above. The ordinary differential equation used is;

$$\frac{dC_C}{dt} = k_C C \tag{8}$$

Where C is the color of mango fruit; and k_C is the rate constant and depend on temperature through an Arrhenius relationship.

Total Soluble Solid Change Modeling. During storage starch is hydrolyzed and break down to hexose sugar by amylase enzyme and hexose units are converted to carbon dioxide and water [9]. As fermentation during commercial storage is avoided and only aerobic respiration is considered.

$$S + E_{amy} \xrightarrow{k_{star}} \text{Hexose Sugar} + 2E_{Amy} \quad (9)$$

$$\text{Hexose Sugar} + 6O_2 \xrightarrow{k_{resp}} 6CO_2 + 6H_2O \quad (10)$$

where S is the amount of starch; E_{amy} is the amount of the amylase enzyme; and k_{star} is the rate of conversion of starch to hexose sugar. It is assumed that percentage of brix measured is related to the hexose sugar concentration according to the following equation

$$Brix = Hexo \quad (11)$$

$$\frac{d[Brix]}{dt} = \frac{d[Hexo]}{dt} = k_{star}\left[E_{amy}\right] - k_{resp}[Hexo] \quad (12)$$

$$\frac{d\left[E_{amy}\right]}{dt} = k_{star}\left[E_{amy}\right] \quad (13)$$

Rate dependency on temperature. Arrhenius model was used to model the dependency of the different rate constants for all the three qualities with temperature [1].

$$k_i = k_{i,ref}\exp\left(\frac{E_{a,i}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \quad (14)$$

Where k_i is the rate constant of the reaction; $k_{i,ref}$ is the rate constant at the reference temperature; $E_{a,i}$ is the activation energy for the reaction; R is the universal gas constant and T is the temperature.

3 Results and Discussion

The measured firmness data are plotted in the figure below together with the corresponding simulated model results. Four model parameters were estimated by the simulation with acceptable standard errors and confidence interval of 87.58% which means that the variation in the measured data of the firmness could be explained by the model. The firmness of mango fruit at all conditions decreases significantly during the storage period but the extent is higher at higher temperature. Slow firmness drop was observed at 7 °C but due to the occurrence of chilling injury mango cannot stored at this temperature for a long period of time. Due to this 13 °C is the optimum temperature to store Ethiopian Kent mango fruits which is also observed in other mango cultivars [3]. The result in Fig. 1 also shows high rate of firmness loss at the beginning of the storage period and slows down after one week period which may be related to an increase in ethylene formation. Fast firmness drop and lower shelf was obtained at room temperature but this loss relatively decreased at 13 and 7 °C.

As it can be easily inferred from the figure the firmness change as a function of temperature can be used to determine the optimum time-temperature storage conditions

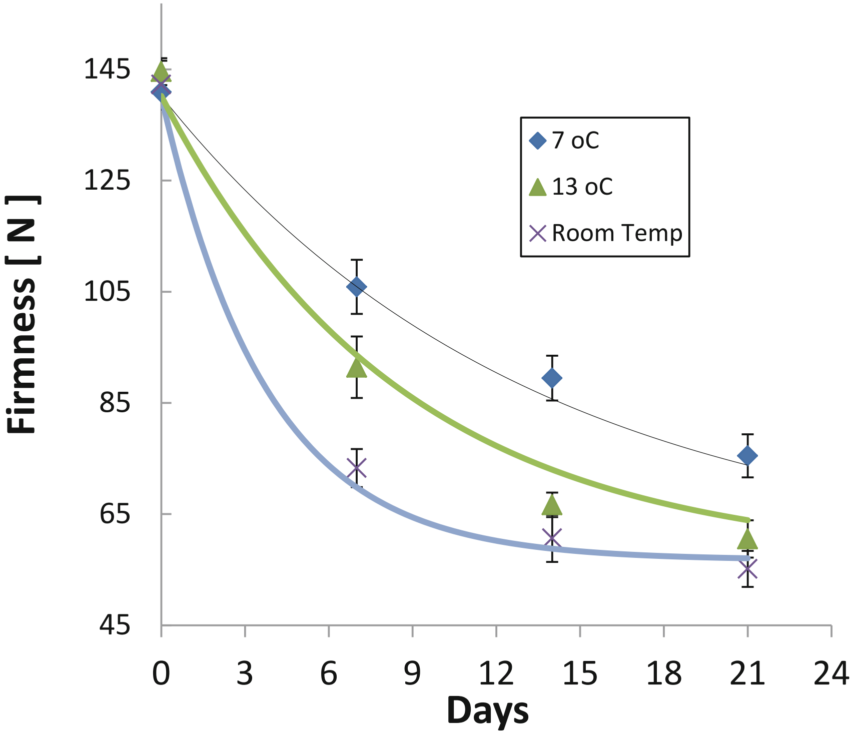


Fig. 1. Firmness of mango fruit during storage at 7, 13 °C and room temperature for storage durations of 21 days. The lines represent the model, and the points are the mean of the measured values.

to handle mango fruit. The evaluation of quality and prediction of postharvest life of mango fruit is a significant means in the handling of the fruit throughout the supply chain [3]. Overall, the fruit used in the present study stored at 7 °C had a longer shelf life compared with those stored at higher temperatures had a shorter shelf life.

After harvest, mango and other fresh fruit undergo continuous changes in color as part of the normal ripening and senescence. Ripening may be desirable in that it makes the fruit palatable, but it limits the storage life of the fruit. The measured color data are plotted in the Fig. 2 together with the corresponding simulated model results. Model parameters were estimated by the simulation with acceptable standard errors and confidence interval of 91.62% which means that the variation in the measured data of the color could be explained by the model. As observed in the figure color change increase from stage 1 to stage 5 at higher rate at high temperature and lower rate at low temperature. This may be due to chlorophyll breakdown, the rate of which was dependent on temperature and ethylene concentration. The change of flesh color is relatively rapid at the start of the experiment but slows down later.

The measured TSS data are plotted in the Fig. 3. together with the corresponding simulated model results. Model parameters were estimated by the simulation with acceptable standard errors and confidence interval of 88.63%. TSS was high in fruits

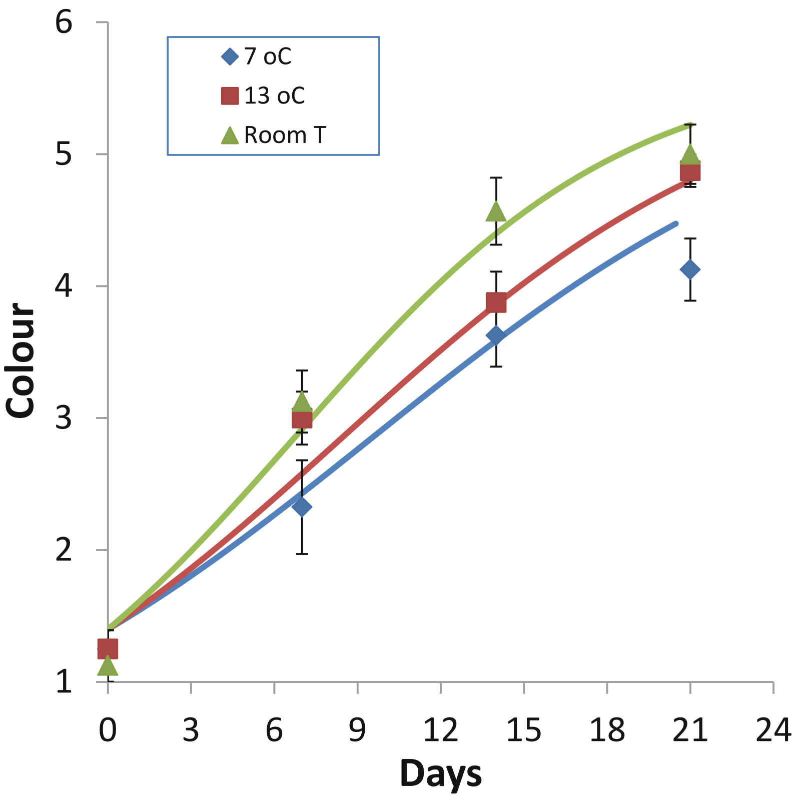


Fig. 2. Color change of mango fruit during storage at 7, 13 °C and room temperature for storage durations of 21 days. The lines represent the model, and the points are the mean of the measured values (Color figure online).

stored with ambient temperature, next fruits stored at 13° C and minimum TSS was observed fruits sored at 7 °C during three weeks of storage. After developing the model for predicting firmness, colour and total soluble solids a ripening stage are assigned from 1 to 5 as shown in the Table 1. with the corresponding quality values; where 1 is the mature green and 5 is the over ripe stage. For each temperature, a limiting quality factor [3] was established considering the rating value of 3 as the maximum acceptable quality before the fruit becomes unmarketable [4]. More specifically, for each temperature, the factor that limited the product marketability was identified from the quality curves.

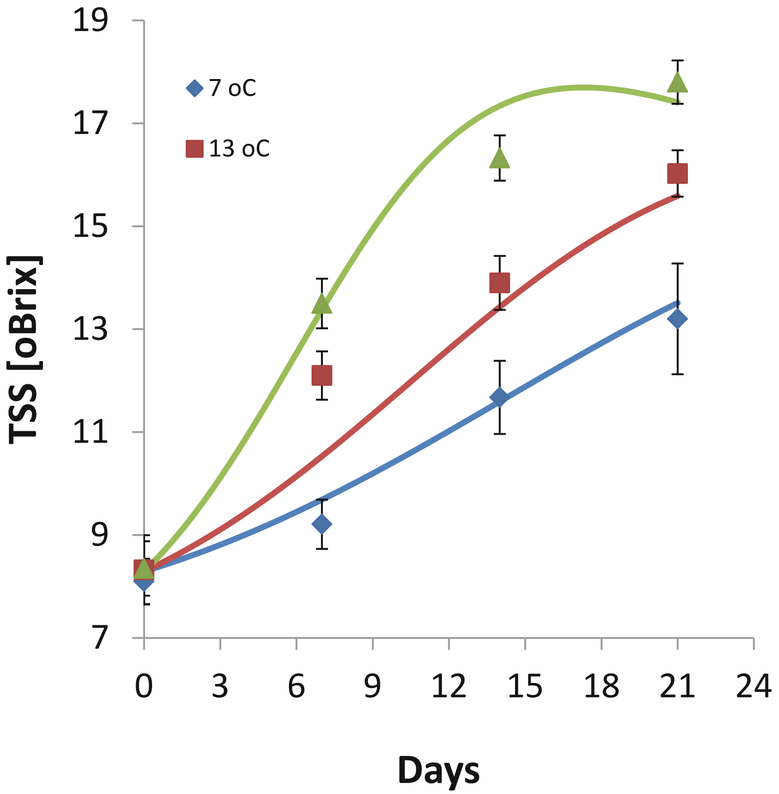


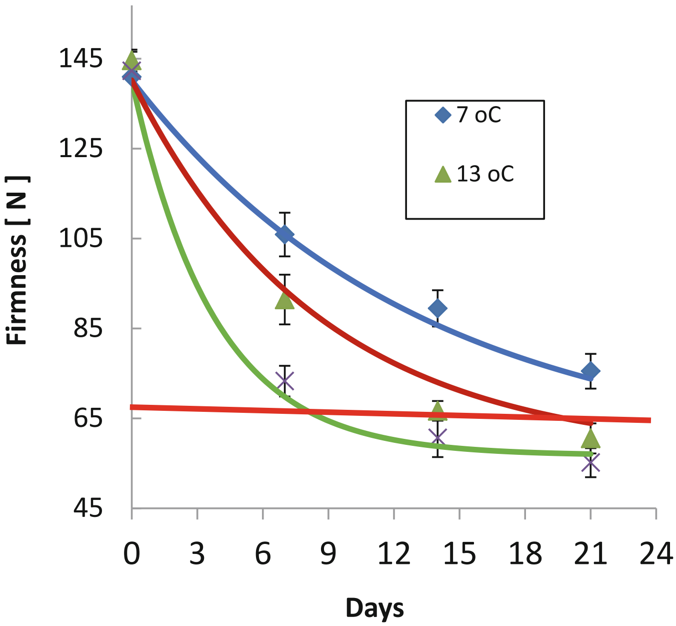
Fig. 3. Total soluble solids of mango fruit during storage at 7, 13 °C and room temperature for storage durations of 21 days. The lines represent the model, and the points are the mean of the measured values (Color figure online).

From these curves it was observed that a single quality factor cannot be used to express the loss of quality of mangoes over the storage period. As it can be easily inferred from the graph softening was the limiting quality factor for mango stored at

Table 1. Average seven-eighths cooling time for mangoes inside different packages.

Ripeness stage	Stage	Flesh color	Firmness (kg/mm2)	TSS
Mature green	1	Very light yellow	>14	>17
Partially ripe	2	Light yellow	10–14	15–17
Full ripe	3	Yellow-light	6–10	12–15
Soft ripe	4	Yellow-orange	2–6	9–12
Over ripe	5	Golden orange	<2	<9

7 °C and color was the limiting quality factor for mango stored at 13 °C and room temperature (Fig. 4).



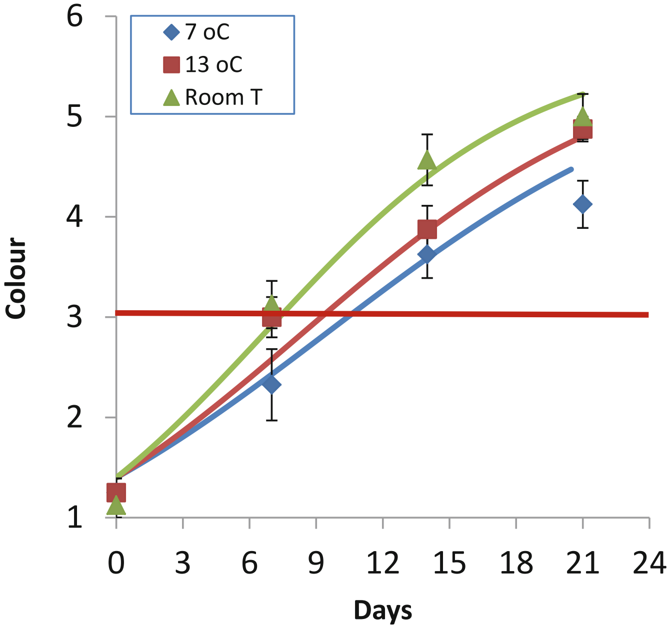


Fig. 4. Quality characteristics of Kent mango fruit stored at 7, 13 °C and room temperature. The red horizontal line represents the maximum acceptable quality (rating ~ 3).

4 Conclusion

Kinetic model was developed for predicting relationship between storage and shelf life conditions and mango quality attributes. Significant quality changes were observed under the three temperature storage conditions which show the effect of temperature on quality parameters. The firmness of mango fruit at all conditions decreases significantly during the storage period but the extent is higher at higher temperature. Slow firmness drop was observed at 7 °C but duse to the occurrence of chilling injury mango cannot stored at this temperature for a long period of time. Softening was the limiting quality factor for mango stored at 7 °C but color was the limiting quality factor for mango stored at 13 °C and room temperature. The Ethiopian mango supply chain from harvest to consumer is expected to take between 15–19 days. So using a cold chain throughout the chain is a must to keep the quality of mango fruit to the standard and in order to avoid the variable quality of mango on arrival in overseas countries. As a result single quality factor cannot be used to express the loss of quality of mangoes over the storage period at variable temperature. Further analysis is recommended to use the quality model for dynamic temperature which needs to determine the validity of the model with such storage conditions. It is also possible to improve the accuracy of the quality model by doing the measurements at shorter time interval and including other cultivars and maturity stages.

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