MODELLING THE FIRMNESS OF 'ELSTAR' APPLES DURING STORAGE AND TRANSPORT

L.M.M. Tijskens, A.C.R. Van Schaik
and M.L.A.T.M. Hertog
ATO-DLO, P.O. Box 17
6700 AA Wageningen
The Netherlands

A. de Jager
Proefstation voor de Fruitteelt PFW
Wilhelminadorp
The Netherlands

Abstract

A dynamic model has been developed that describes the decrease in firmness of 'Elstar' apples during different types of conditions, based on the general knowledge how firmness is affected by chemical and biochemical reactions, and on the strict and consistent application of fundamental kinetics.

The variable part of the firmness of apples is deduced to depend mainly on the pectic compounds in the middle lamellae. These pectic compounds are supposed to decay during storage in two distinct routes, one consuming/needing oxygen and one occurring with or without oxygen.

Depending on the gas conditions (oxygen and carbon dioxide) the respiration rate of apples change. This respiration affects the rate of the oxygen consuming pectin degradation. The moment of harvest defines among other, the initial climacteric stage of the apples. Depending on the relative respiration rate, the rate of development of the climacteric stage changes. The climacteric stage in itself affects the rate of pectin decay: preclimacteric apples can be kept longer than climacteric ones.

During CA or MA storage, an enzyme, probably polygalacturonase, accumulates depending on the length of the CA/MA period: the longer kept at CA/MA conditions, the faster firmness decays at the end of the storage period.

On top of all those interactions, a temperature dependence is applied on all individual reaction rates. This temperature dependence is described by the well know Arrhenius law. The model can be applied to predict the firmness of 'Elstar' apples during all kinds of scenarios encountered in practice, to get an impression of the expected final firmness when reaching the consumer.

1. Introduction

The behaviour of firmness of apples is and has been subject of study for already a long time. Knowledge about this behaviour has been emerging from these studies almost as long. Compilations of this kind of information invariably result in very informative and long monographs (e.g. Thompson 1996). This knowledge has, however, never been interpreted using one consistent and multidisciplinary philosophy. In this lecture a model is described, attempting to combine the knowledge available into a mathematical and dynamic formulation.

The effects covered by the model include time of storage, temperature and ethylene during storage, as well as the effect of harvest maturity. The model is not validated in the classical sense of the meaning, but checked against the expert opinion of long time apple storage and quality researchers.

2. How is firmness built up?

The quality attribute firmness of agricultural products can be regarded as the way human beings can detect the physico-mechanical properties of these products. The texture of agricultural products is built up by a combination of the physical forces originating

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from the following processes or properties that generate strength upon compression or chewing:

- turgor pressure inside intact living cells, creating a tissue tension;
- special compounds / granules inside the cell possibly generating strength (e.g. starch);
- cohesive forces within a cell, generated by chemical composition and physical properties of the cell wall;
- adhesive forces between cells, generated by chemical composition and physical properties of the middle lamellae and the pectin chains;
- overall structure and shape of separate cells (cell dimension and contact area);
- overall structure and shape of tissue, like strength and distribution of vascular tissue.

In this overview, the first four items represent the chemical and physical based forces, the last two items represent the histological and morphological ones (archestructure). Within the textural behaviour of a particular fruit, all these aspects are more or less present and heavily interacting. Depending on relative occurrence and importance of the mentioned items, a very diverse range of observed behaviour of texture and firmness can be depicted, e.g.:

- with only turgor or tissue tension as the major item, products are soft and juicy, losing texture upon processing like strawberries;
- with pectin forces overruling, products are essential crispy and juicy (rupture through cells with release of juice from the disrupted cells) like fresh apples;
- with cell wall forces overruling, products are essential mealy and dry (rupture along cells without release of juice from the intact cells) like sometimes senescent apples;
- with vascular tissue important, products are essential tough and fibrous like sometimes in asparagus.

3. How does firmness change?

Each process and each property mentioned in previous paragraph can and will have its effect on the observed firmness of any product, including apples.

Structural aspects and special compounds inside the cell are predominant in determining the type and the level of firmness in any fruit, but will most probably not (much) change during storage (e.g. cell shape and elasticity of the primary wall) as can be taken from the same firmness remaining after storage at different temperatures (see Fig. 1, Thompson 1996). These structural aspects exhibit a cultivar specific but standard developmental pattern during growth (Fry 1988).

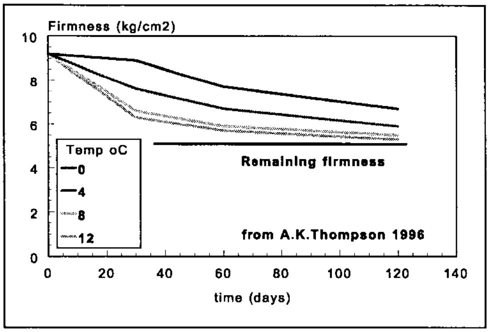

Figure 1. Pattern of behaviour of apple firmness during storage at different temperatures

Pectin may decay by enzymatic action of pectin methyl esterase (PE) and of polygalacturonase (PG) (Keijbets 1974, Voragen and Pilnik 1989). PE activity decreases the degree of methylation of the pectin chain (Rodis *et al.*, 1997, Tijskens *et al.*, 1997b, 1997c). PG decreases the length of the pectin chain (Tijskens *et al.*, 1997a). So, both enzymes primarily affect the middle lamellae and hence the strength of the cell-cell adhesion.

Water loss will affect the turgor and the tissue tension. So, during storage, firmness will only change by the last two processes. The invariable properties are induced by cellulose composition of the cell wall, overall cell size, cell structure, vascular tissue and special compounds inside the cells. They most probably do not change much at normal storage conditions. They contribute, however, for the major part to the existence of the firmness remaining even after prolonged storage (Tijskens 1979).

A model describing firmness behaviour of apples has consequently to be founded in a vast simplification, with as little violation of the real world system as possible. It will not be as comprehensive on a detailed compositional basis as, e.g. Carpita and Gibeaut (1993). It has, however, to be much more comprehensive with regard to completeness of important processes involved in a multidisciplinary approach, combining physical, chemical and biochemical effects on the observed firmness. The rates of the □selected□ processes will depend on the actual conditions during ripening and storage with respect to temperature, relative humidity, gas conditions (O_2, CO_2, ethylene) and the actual levels of several enzyme activities.

The effects of water loss on the firmness of apples will not be further discussed in this paper.

4. Model formulation

The basic processes occurring during growth (Sfakiotakis and Dilley 1973), included in the mathematical model, are:

- ripening at the tree including the on tree ripening inhibition process;
- *development of climacteric stage.*

As there is not much information on the exact nature and mechanisms for these processes, which are actually the same, they are described by an empirical logistic (sigmoidal) curve. This reflects roughly the general experience with respect to ethylene dose-responses and on-tree ripening (Lau *et al.* 1986, De Pooter and Schamp 1989).

The basic processes included in the mathematical model occurring during storage are:

- pectin decay affected by O_2;
- pectin decay without effect of O_2;
- moisture loss.

The two types of pectin decay are generally not recognised as such in literature. Tijskens indicated already in 1979, that the general pattern of firmness decrease could be regarded as the result of two pectin decay processes (Eq. 1).

$$\text{Pect} \xrightarrow{k_p} \text{decay}$$

$$\text{Pect} + O_2 \xrightarrow{k_p} \text{decay}$$

Formulation of the mechanism as shown, does not imply that this is the exact nature of the processes going on in the fruit, which is probably a system of enzymatic reactions involving PE and PG, but merely that the phenomena observed can be explained, by simplifying the actual processes into this mechanism. The first one always occurs, regardless of the gas conditions applied, the second process needs oxygen to proceed, and will consequently be slowed down by CA conditions (see the paragraph: Effects of CA conditions).

5. Effects of temperature

All rates of chemical and biochemical reactions depend on temperature. In the model formulations, the relation given by Arrhenius' equation (Eq. 2) is used throughout for each reaction rate constant:

$$k_i = k_{i,ref} \; e^{\frac{Ea}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)}$$

This not only includes the pectin degrading reactions, but also the effects of ethylene, respiration, ripening (climacteric stage) and senescence. The energy of activation (Ea) is a measure for the susceptibility of that reaction for temperature. Each reaction rate constant has its own specific dependence on temperature, expressed in the energy of activation. This explains the sometimes observed difference in relative importance of different reactions / processes at different temperatures.

6. Effects of CA and MA conditions

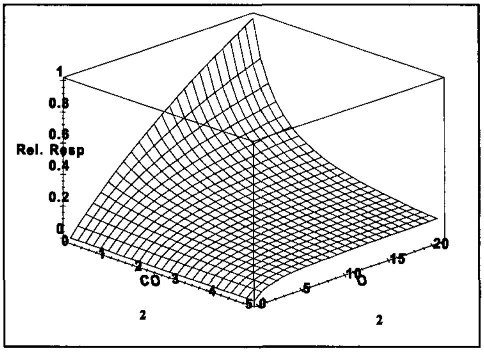

Figure 2. Relative respiration in 'Elstar' apples as simulated by the model

Applying low oxygen and high carbon dioxide levels in the storage rooms is already long time recognised as a valuable tool in increasing the storage potential or keeping quality of apples. It is generally assumed that it acts by slowing down (almost) all chemical and biochemical reactions occurring in the product. According to Solomos and Kannelis (1989) and Kanellis *et al.* (1993) the effect of oxygen level or respiration intensity is different for different reactions. There is, however, not much numerical information on this subject. Recently, some models came available (Peppelenbos *et al.*, 1993, 1996, Hertog *et al.* 1997) that describe the intensity of the respiratory processes as a function of O_2, CO_2 and temperature. The general formulation was used to develop, for aerobic situations, a relative respiration (Tijskens 1995). Relative respiration is the ratio of the respiration intensity at any temperature and gas condition, to the respiration intensity at the same temperature in air (Eq. 3).

$$\text{RelResp} = \frac{O_2}{21} \; \frac{1 + K_{mo} \; 21}{1 + K_{mo} \; O_2 + K_{moc} \; O_2 \; CO_2}$$

This relative respiration proved to be more or less independent of temperature, and can consequently be used to separate the effects of gas condition from the effects of temperature. On figure 2 an example is shown for the behaviour of relative respiration as a function of the applied O_2 and CO_2 levels in 'Elstar' apples. The relative respiration is used in the model to modify the rates of some of the processes like that type of pectin decay that needs oxygen, and the development of the climacteric stage.

During CA and/or MA storage a second process is occurring. The longer CA storage takes places, and the more intensive (the lower the relative respiration) the faster firmness decay will be when putting the product again at normal conditions (air and room temperature). This is modelled as the accumulation of an enzyme (maybe PG, more probably related to ACC production and accumulation) that enhances pectin decay in the ex-store life.

$$\frac{\partial PG}{\partial t} = k_{PG}\, PG$$

The oxygen induced decay of apple pectin than becomes:

$$\frac{\partial \mathrm{Pect}_{pO}}{\partial t} = -\; k_{pO}\ \mathrm{Pect}_{pO}\ \mathrm{PG\ RelRep} \\ +\; k_{pO}\ \mathrm{Pect}_{pO}\ (1\ -\ \mathrm{RelResp})$$

This formulation, however, is too empirical and most probably an incorrect representation of the processes involved. Studies to correct this situation are being conducted.

7. Effects of harvest maturity and ethylene

The effect of ethylene on pre- and postharvest behaviour of apples has been modelled with an empirical function. It is assumed that ethylene induces ripening at the tree and during storage pretty much in the same way, except for the on tree ethylene inhibition. Production of ethylene is modelled as the derivative of the well-known logistic curve:

$$\frac{\partial \mathrm{Eth}}{\partial t} = k_{\mathrm{eth}}\ \mathrm{Eth}\left(1\ -\ \frac{\mathrm{Eth}}{\mathrm{Eth}_{\mathrm{max}}}\right)$$

The action exerted by this amount of ethylene is proportional to the integral of this function, again taking the variable temperature during all kinds of actions into account. The time in this equation is somewhat ambiguous. In postharvest research and postharvest practical applications, we are used to start counting the time from the moment the food chain begins, which is usually the moment of harvest. To obtain an initial level of ethylene, necessary with this oversimplified logistic function, the moment of harvest has to be expressed relative to a fixed point in time, let's say the optimal harvest time.

The climacteric stage of the product, both preharvest and postharvest, depends on the history of ethylene production and action. On his turn, the climacteric stage, expressed as a fraction of the maximal climacteric stage, affects a number of processes like pectin decay.

8. Chain simulation - a practical application

The model describes the behaviour of firmness based on the processes possibly occurring in any part of the lifespan of an apple, from growing over harvest to storage and transport. The model can now be applied to predict the firmness in any known or unknown scenario of temperature and applied gas conditions, from any starting point with regard to maturity at harvest or growing condition.

Optimisation of complete chains of product handling with respect to the expected firmness becomes feasible. The optimisation itself has, for the time being, to be conducted by hand. Compiling this model into a computer initiated optimisation requires a more validated model to permit such an effort.

In the next figures some examples are given for the prediction of firmness of 'Elstar' apples during various scenarios and harvest maturities.

Example 1: variable temperatures.

In figures 3 to 6 a scenario was applied to apples with a harvest maturity of 18 days before climacterium, with in total 1.5 days at 20°C in air to simulate harvest, transport and auction before commercial storage, followed by a commercial storage at 1 to 6°C in an atmosphere of 1 % O_2 and 3% CO_2 at a relative humidity of 90%.

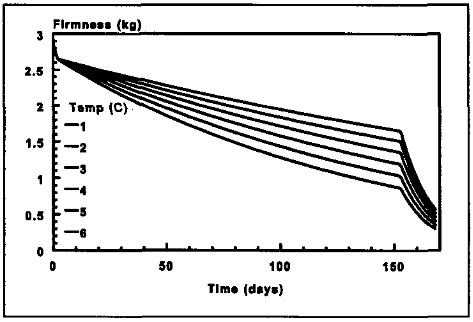

Figure 3. Firmness during storage and ex-store life at different storage temperatures

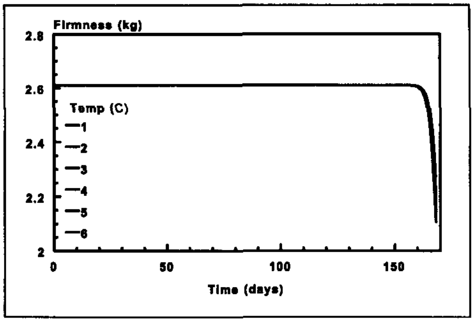

Figure 4. Firmness generated by oxygen-sensitive pectin decay

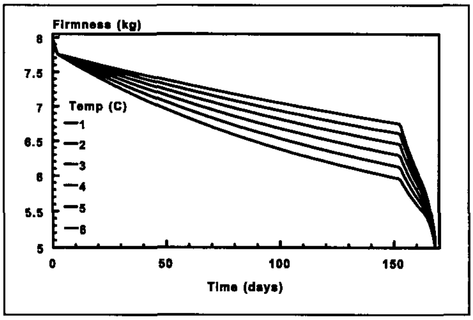

Figure 5. Firmness as generated by oxygen-insensitive pectin decay

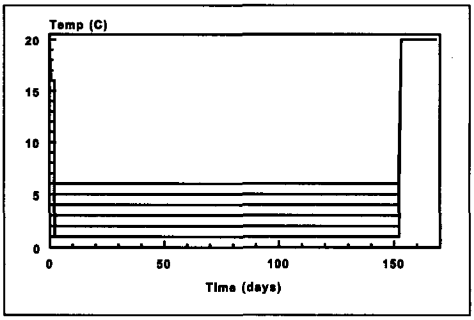

Figure 6. Temperature scenario during storage and ex-store life

The effect on firmness decay by different storage conditions can clearly be seen. Also it should be noted that the firmness only decreases by action of the pectin decay that does not need oxygen (Fig. 4 and 5). Also can be noted the (small) difference decrease in rate of firmness decrease during the ex-store period of 15 days at 20°C, which is a simulation of the shelf-life at the consumers.

Example 2: Variable harvest maturity

In the same chain setup as in example one, apples with a harvest maturity from 25 to 0 days before reaching the climacteric stages, were stored at 1°C in 1% O_2 and 3% CO2. In the next figures, the simulated behaviour is shown.

The effects of harvest maturity are dramatically visible on figure 9 showing the development of the climacteric stage. The riper the apples are at harvest, the sooner climacterium is reached, even in CA conditions. The effects on firmness during storage are not that dramatic, but the firmness decreases considerably faster during the shelf life of the product the riper the apples were harvested.

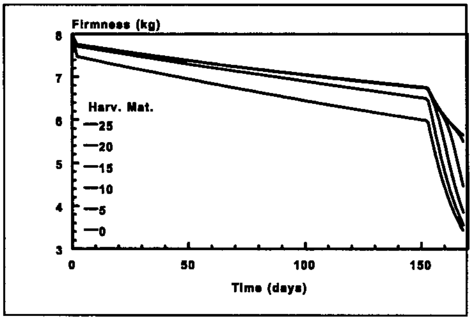

Figure 7. Firmness as affected by maturity at harvest

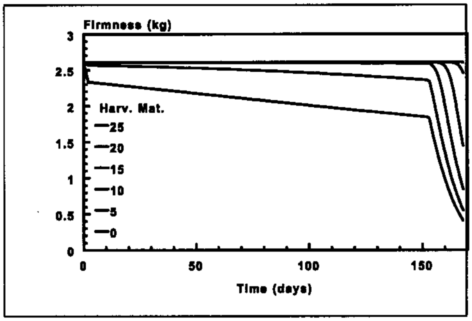

Figure 8. Firmness generated by oxygen-sensitive pectin decay

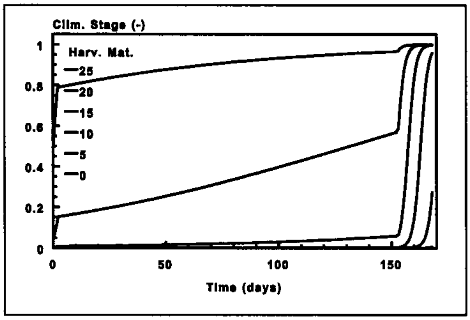

Figure 9. Development of climacteric stage for different maturities at harvest

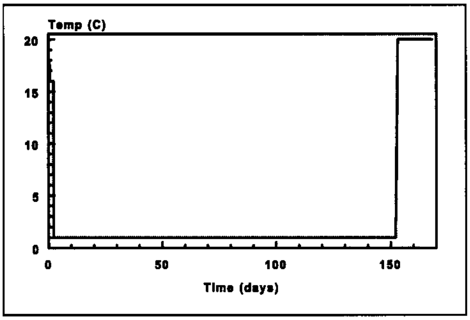

Figure 10. Temperature scenario for apples with different maturities at harvest

9. Conclusions

Predictions can be made by mathematical simulation of the behaviour of firmness of 'Elstar' apples during all kinds of storage and transport scenarios. The model structure is more based on the processes involved than on the observed phenomena. The modular structure of the model provides information about the effects of the conditions applied in the chain of the individual constituting parts of firmness.

It should be noted that using modelling, the exact prediction of firmness itself is very difficult. The major advantage of simulation research is to be found in indicating trends in product behaviour upon a change in scenario applied.

References

Carpita, N.C. and Gibeaut, D.M., 1993. Structural models of primary cell walls in flowering plants: consistency of molecular structure with the physical properties of the walls during growth. The Plant J. 1: 1-30.

De Pooter, H.L. and Schamp, N., 1989. Involvement of lipoxygenase - mediated lipid catabolism in the start of the autocatalytic ethylene production by apples (c.v. Golden Delicious: a ripening hypothesis. International Symposium on Postharvest Handling of Fruits and Vegetables, 29 Aug.-2 Sep. 1988, Leuven, Belgium, Acta Hortic. 258: 37-46.

Fry, S.C., 1988. The growing plant cell wall: chemical and metabolic analysis. Longman Scientific and Technical, Harlow, Essex.

Hertog, M.L.A.T.M., Tijskens, L.M.M., Peppelenbos, H.W. and Evelo, R.G., 1997. Modified atmosphere packaging: Optimisation through simulation. Seventh International Controlled Atmosphere Research Conference, July, Davis, USA (*in press*).

Kanellis, A.K., Loulakakis, K.A., Hassan, M.M. and Roubelakis-Angelakis, K.A. 1993. Biochemical and molecular aspects of low oxygen action on fruit ripening. In: Pech, J.C., Latché, A. and Balagué C. (eds), Proceedings of the International Symposium on Cellular and Molecular Aspects of Biosynthesis and Action of the Plant Hormone Ethylene, August 31-September 4, 1992, Agen, France. Kluwer Acad. Publ., Dordrecht, NL. pp. 117-122.

Keijbets, M.J.H., 1974. Pectic substances in the cell wall and the intercellular cohesion of potato tuber tissue during cooking. Proefschrift Landbouwhogeschool, Afd. Levensmiddelentechnologie, Wageningen, IBVL-publicatie nr. 275.

Lau, O.L., Liu, Y. and Yang, S.F. 1986. Effects of fruit detachment on ethylene biosynthesis and loss of flesh firmness, skin color, and starch in ripening □Golden Delicious□ apples. J. Am. Soc. Hort. Sci. 111: 731-734.

Peppelenbos, H.W., Van 't Leven, J., Van Zwol, B.H. and Tijskens, L.M.M., 1993. The influence of O_2 and CO_2 on the quality of fresh mushrooms. Proceedings, Sixth International Controlled Atmosphere Research Conference, Ithaca, June 15-17, USA, pp. 746-758.

Peppelenbos, H.W., Tijskens, L.M.M., van 't Leven, J. and Wilkinson, E.C., 1996. Modelling oxidative and fermentative carbondioxide production of fruits and vegetables. Postharvest Biol. Technol. 9: 283-295.

Rodis, P.S., Polisiou, M. and Tijskens, L.M.M., 1997. Relationship between degree of pectin esterification measured by FT-IR and tissue firmness of Redhaven peaches. Proceedings COST 915 and COPERNICUS/CIPA workshop Food Quality Modelling, June, Leuven, Belgium. (*in press*).

Sfakiotakis, E.M. and Dilley, D.R., 1973. Induction of autocatalytic ethylene production in apple fruits by propylene in relation to maturity and oxygen. J. Am. Soc. Hort. Sci: 98: 504-508.

Solomos, T. and Kanellis, A. 1989. Low oxygen and fruit ripening. International symposium on Postharvest Handling of Fruits and Vegetables, 29 Aug.-2 Sep. 1988, Leuven, Belgium, Acta Hortic. 258: 151-160.

Thompson, A.K., 1996. Postharvest Technology of fruits and vegetables. Blackwell Science Ltd, Oxford, UK.

Tijskens ,L.M.M., 1979. Texture of Golden Delicious apples during Storage. Lebensm.-Wiss. U. -Technol. 12: 138-142.

Tijskens, L.M.M., 1995. A model on the respiration of vegetable produce during postharvest treatments. Proceedings International Conference on AGRI-FOOD Quality, June 1995, Norwich, United Kingdom, pp. 322-327.

Tijskens, L.M.M., Hertog, M.L.A.T.M., Rodis, P.S., Kalantzi, U. and Van Dijk, C., 1997a. Kinetics of polygalacturonase activity and firmness of peaches during storage. J. Food Eng. (submitted)

Tijskens, L.M.M. and Rodis, P.S., 1997b. Kinetics of enzyme activity in peaches during storage and processing. Food Technol. Biotechnol. 35: 45-50.

Tijskens, L.M.M., Waldron, K.W., Ng, A., Ingham, L. and Van Dijk, C., 1997c. The kinetics of pectin methyl esterase in potatoes and carrots during blanching. J. Food Eng. (submitted)

Voragen, A.G.J. and Pilnik, W., 1989. Pectin degrading enzymes in fruit and vegetable processing. In: Aspects of Enzymes Chemistry for Agriculture. ACS symposium Series 389. American Chemical Society ACS, New York, pp. 93-115.