Cooling Technology: Why and How utilized in Food Processing and allied Industries

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Module No 11

Lecture 55
Control Atmosphere Storage

So, good morning my dear students and. Friends who are in the class, we have started with the application already we have done one of such that is freezing. Now, we come to another application that is called controlled atmosphere storage, right. So, in this controlled atmosphere (CA) storage, we do like this, that the ok, these are some information, like status of the Indian, typically Indian fruits and vegetables production, and obviously, its maintenance and definitely India waste more fruits and vegetables than are consumed in many small countries. In European countries, if you few see that, many countries are even smaller than say, West Bengal, or say Gujarat, or any such, right. So, there, whatever, our production being so high, and our population being so high, consumption is also definitely little high, but wastage is also very high, and this wastage is not that you are buying and throwing it out.

It is at the, not buyers end, at the producers end, because, of the non availability of the proper storage facilities, this wastage is a part right. Now, obviously, remedy could be that, efficient storage and distribution system, if you can have. If you also can have cold chain, this cold chain will also say sometime, may be in the last class, when ice cream will be covering up. Post-hustle based management, that is, the prime, and in that one, such remedy could be, use of controlled atmosphere storage, and to do that, a new thing, which, for you is, rate of respiration, to know that, in earlier class, perhaps while we were calculating the load of the refrigeration, there, we have been talking all, we have taken this rate of respiration as load, right.

Obviously, this rate of respiration is associated with the ripening of the fruits, right. Obviously, we have not seen vegetables getting ripened. It is fruits, and that too, there are not all the types of fruits, which are ripened. I don't know, I afterwards, I will get this scope or not. Let me say one thing here that, if you see the rate of ripening, sorry, rate of respiration with time, this being time, then there will be a graph like this, and coming out like this. This typical curve is known as the respiration curve, or climacteric curve.

I write here, C L I M A C T E R I C, climacteric curve, right. There are some fruits, and fruits rather, which are climacteric in nature, some fruits which are not climacteric in nature. For example, if you take guava, I am sorry, not guava, if you take cucumber, it can be taken either as fruit or as vegetable. So, you have not seen that, cucumber, you have taken and the colour, whatever it has, it got changed. Yes, with time it may shrunken, or it may get damaged, etc., but it did not change the colour, unlike, if you have mango, right.

Mango, which is green in colour, and when it got ripened, it is yellow in colour, one of the best example of ripening, right. So, we can now say that, once you have the remedy, then we should also know why fruits spoil, right. The deterioration of fruit is associated with the physicochemical and biochemical activities, and the living cells of harvested plant products respire continuously utilizing oxygen from the surrounding environment and releasing carbon dioxide. In general, there is an inverse relationship between respiration rate and the storage life, and produced with no respiration rate, generally, have longer shelf life. This is what I was referring to, right.

So, this is rate of respiration, or rate of oxygen consumption, by which, we say that rate of respiration, this is rate of oxygen consumption with time. So, you see, it is coming down going up and then this is the starting. We have harvested from the tree that, the mother plant, who was supplying all energy everything to the fruit. Now, when you have taken out from the tree, so, all supply is over, now it is on its own. So, to acclimatize with the new circumstance, the fruit materials take up oxygen, or rate of respiration goes down, and when it gets acclimatized, it starts again taking up and at the end, at the rise, where ripening is maximum, this period is known as ripening period right.

When, it becomes maximum, right, that is, the maximum ripening, after that, it starts deteriorating, or decaying, right. So, this is what. Now, in our respiration, or in our shear storage, or control atmosphere storage, if this we call, R and if this we call T, time, right, the main purpose is to elongate this as much as you can, right, as if, you have a, you have a string of thread, which you can elongate, like this. So, that is what actually CA will do, or does, right. You are elongating the rate of respiration to the extent you can, right.

So, that is the basic of the CA storage. Now, you are talking about, why fruit ripens? Right, and how it ripens? So, this is what I was referring to that mango, which you have harvested from the tree, and it is green in color, it has acid, it has starch, it has chlorophyll, it has pectin, as hard pectin, large organic substances, there. So, while ripening, that process, while ripening that process, let us go back to this. In this process, that is, what we were referring to, this, during this process, that, all this green part is gradually converted to yellow part.

How? that is what we were showing you, how it is getting converted. So, the acid, starch, chlorophyll, because of which, it is green, then pectin, because of which, it is hard, if you buy raw mango, you will get it, to be hard, large organic compounds, are there, sorry, large organic compounds are also there. So, what it is doing? There are lots of enzymes, like kinase, like amylase, like hydrolase, like pectinase, like hydrolases, and many others are there. So, what do they do? They convert this acid to neutral condition, they convert starch to sugar, they convert chlorophyll to anthocyanin, which is yellow in color, and also the pectin, hard, is converted to less pectin with soft pectin type, in pectic substances you will see this. I have taught in detail in my another class, which is also in NPTEL, you just find out, which is also available in LPTEL. So, they are less pectin, which are soft, and what I was referring to that, pectic substances, there are many types, protopectin, pectin, then pectinic acid and many others.

So, some of which are hard in nature, some of which are soft in nature. You take everyday bread, butter, jam, jelly, right in that jam, jelly, pectin is there, right, pectin is there for binding, it is one of the constituents, right. So, that is converted into less pectin or soft pectin, and the large organics, which are present there, they are converted into aromatic substances, and that is why, if you buy mango, and ripen it, if it is even at one corner of the room, from the other corner of the room, you will find that, yes, in this room mango has come, ripen mango, right. So, that is what, it is converted into, sorry, into different aromatic substances. So, we can say that, sometimes, say, wound will cause rapid ethylene production also. This means, picking a fruit will sometimes signal. So, you are picking one fruit from the tree.

So, it gives a signal to ripen and infection of bacteria or fungi rather on the fruit, can also do the same job, and this ethylene signal causes development, developmental changes that result in fruit ripening. So, what happens during ripening? New enzymes are made, because of the ethylene signal, and if you ask your parents, or those who go to the market, they know that, unripened fruits, they keep in with carbide, that is why, most of the time, you hear this, that it is ripened with carbide, right. There acetylene, that is C_2H_2, acetylene, that is CH triple bond CH, this is acetylene. So, when water and acetylene they are together, then ethylene, that is, C_2H_4, that is, C_2H_4 is produced, right, and that is what? CH_2 double bond CH_2, right. So, this is carbon and this is double bond ok.

So, acetylene or carbide formation or carbide ripening are also done, and that is because of the production of acetylene, sorry, ethylene. So, new enzymes are made, because of the ethylene signal, and these include hydrolases to help break down chemicals inside the fruits, right, and amylases, to accelerate rather, amylases, to accelerate hydrolysis of starch into sugar, pectinase, to catalyze pectinase, to catalyze degradation of pectin, and so on. Ethylene apparently turns on the genes that are then transcribed and translated to make these enzymes. The enzymes then, catalyze reactions to alter the characteristics of fruit. The action of the enzymes, cause the ripening responses. Chlorophyll is broken down and sometimes, new pigments, new pigments are made, so that the fruit skin changes color from green to red or yellow.

Acids are broken down, so that, the fruit changes from sour to neutral. The degradation of starch by amylase, produces sugar, and this reduces the mealy, that is, flowery quality, and increases juiciness. The breakdown of pectin by pectinase between the fruit cells unglues them, so, they can slip, past each other, that results in a softer fruit. Also enzymes break down large organic molecules into smaller ones, that can be volatile, that is, that can evaporate into the air, and we can detect as an aroma, which I just said, gave the example of ripened mango, keeping at one corner, and other corner, you are getting it. Now, the question comes, how ethylene is formed, right, how ethylene is formed?

So, S adenosyl methionine, is a precursor for the synthesis of ethylene. The positive charge of the sulphur atom in S adenosyl methionine, that methionine, rather, that enables the cleavage to form cyclopropane. In a reaction catalyzed by amino cyclopropane carboxylate synthase or called ACC synthase, that subsequently, it is oxidized, or it can be oxidized, catalyze the oxidation of the cyclopropane to ethylene, that takes place. Carbon dioxide carbon dioxide, some prusik acid, immediately detoxified by converting to beta, converting to beta cyanoanine, and water, right. So, we are skipping this mechanism, because that, we have already given, you can see from here right.

Now, which one is first temperature, or atmosphere. In control atmosphere storage, which we have not defined as of now. So, let us define that, what is that? It is a system, in which the recommended production of oxygen and carbon dioxide concentrations of storage atmosphere are established, monitored, and maintained throughout the storage period by employing the external means, besides reducing the temperature. In shear storage, the rate of respiration is reduced approximately, 250 percent, compared to normal atmosphere storage, at the same temperature. Thus, doubling the shelf life of the stored produce. So, in this respect, respiration is considered to be the major metabolic process to be reduced in the CA storage, right.

Now, if we go back to what we were saying that, which one is first, that means, we are seeing that controlling temperature and gas composition, these two together is giving us the CA storage. Now, which one is first, temperature or atmosphere, right. Say, in this kind of a big room, where it is a storage one, to change the temperature, it will take lot of time, with the help of vapour compression refrigeration system, right. Obviously, if you do it as we have seen in the freezing, with cryogenic fluids, then it could be done instantly, but, since it is not, and it is only by the vapour compression refrigeration system, then the time requirement will be very high, right. So, in that case the gas composition should be controlled first, so that the changes are limited, but it is better if you can do the temperature first, because we have seen Q_{10}, earlier, right.

If we have seen Q_{10}, earlier, so, if we do that, then perhaps, we can easily control the system ok. Then, how to do this? How to do this, right? Right, how to do this? To do this, we can do flushing with liquid nitrogen, which we have done in our department, some students have done PhDs also. Then you can control both temperature and gas composition, more or less simultaneously, and also the oxygen concentration, or air, whatever it be, right. Obviously, why we are using liquid nitrogen? We say, which, there is a vapour compression refrigeration system, but liquid nitrogen, we are using obviously, to get the temperature rapidly changed, and to control the composition of gas, composition of gas, that is, also rapidly. Now, this is one which, we have done obviously, this is also we have done, and this has been, has already been, I mean protected, right.

So, this is a chamber, and since liquid nitrogen does not come in contact with the fruits directly, so, some steps have been taken, and ultimately, and ultimately totally automatic system has been developed, that is the control of oxygen concentration, carbon dioxide concentration and temperature, these three are automatically done right. Oxygen is allowed to vary between 2 to 5 percent, and similarly carbon dioxide is also varied between 2 to 5 percent. See, when oxygen has become 5 percent, there will be some gas which will be, which will be PURGED out and if carbon dioxide also becomes 5 percent, then there will be some scrubber, by which carbon dioxide is also brought back. Temperature, generally is

now very limited, skipping some this is the product, which we have done, or you can also do, that is lychee which we have done for 2 months or even more.

Then this is how the place where you are keeping, that place has to be tested against pressure drop or leakage, right. according to the available ASTM method we have checked the pressure drop right, we skip this. This is how the respiration rate that we have, we have determined right. So, there is a sensor, this is oxygen, carbon dioxide, nitrogen, analyzer, or meter. So, we have plotted this time temperature, sorry, we have plotted this time temperature changes and there we have seen that it is taking very long time, oxygen uptake or down, right, it is taking very long time to reach from 20 percent to say 2 percent or 5 percent, right. So, in this way, the oxygen uptake or respiration rate is found out, right, and we have plotted how the oxygen is depleting and temperature also is increasing.

Then, the method or respiration rate, this is how we have already shown, this is how it is. It is, there is a, this is called respirometer, right. So, all are tightly sealed, so that no gas can get in or can come out, leak test we have done, right, and this is a DANS sensor method of your monitoring the gas composition, ok. So, this is called closed system method. These are the equations by which R_{O2} respiration rate in terms of oxygen consumption or in terms of carbon dioxide release are determined, and then, how we are changing, this is a schematic diagram for the closed system method right. Respiration rate again respiration rate is also following Michaelis-Menten type of equation. So, that is how we have done right, and this is called enzyme kinetics principles of enzyme kinetics, which we have used right.

So, there could be uncompetitive, competitive, right, non competitive type of relations, right, once you have then, you get the respiration rate, from there you can know how much time you can extend through controlled atmosphere storage? Our time is up. Thank you for listening to us. Thank you. We will meet in the next class.

$$R_{O2} = \left[\frac{(Y_{O2})_t - (Y_{O2})_{t+1}}{\Delta t} \right] \frac{V_f}{W}$$

$$R_{CO2} = \left[\frac{(Z_{CO2})_{t+1} - (Z_{CO2})_t}{\Delta t} \right] \frac{V_f}{W}$$

where: R_{O2} is the respiration rate, ml [O_2] $kg^{-1}h^{-1}$, R_{CO2} is the respiration rate, ml [CO_2] $kg^{-1}h^{-1}$, Y_{O2} and Z_{CO2} are the gas concentrations for O_2 and CO_2 in volume fraction respectively, t is the storage time in h, Δt is the time difference between two gas measurements, V_f is the free volume of the respiration chamber in ml and W is the weight of the fruit in kg.

$$V_f = \frac{Q_N \times 100}{(N_f - N_i)}$$

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where, V_f is the free volume of the respiration chamber in cm^3, Q_N is the volume of N_2 injected into the respiration chamber in cm^3, N_i and N_f are the initial and final N_2 concentration in %.

$$RR = \frac{a * v_m * G_{o_2}}{1 + (a * G_{o_2}) + (a * i * G_{o_2} * G_{co_2})}$$

- ✔ Model based on the Langmuir theory of adsorption
- ✔ suitable for describing O_2 consumption rates in MAP
- ✔ RR = O_2 consumption rate, mmol/kg h
- ✔ v_m = max. O_2 consumption rate, mmol/kg h
- ✔ a,i = rate parameter, 1/kPa
- ✔ G = concentration of respective gases, kPa

Principles of enzyme kinetics

- ✔ The relation between gas consumption and concentration as described by Michaelis Menten type equation
- ✔ Simplified approach assuming one limiting enzymatic reaction instead of all the enzymes involved
- ✔ Generally, found to fit experimental data reasonably well

$$RR = \frac{v_m * G_{o_2}}{k_m + G_{o_2}}$$

RR = O_2 consumption rate, ml/kg h

v_m = max. O_2 consumption rate, ml/kg h

K_m = Michaelis constant for O_2 consumption, % O_2

Note : Above equation assumes no inhibition

Effect of inhibitor - CO_2

1. Competitive

Occurs when both inhibitor and substrate compete for the same site of enzyme. An increase of O_2 at high CO_2 would strongly influence the O_2 consumption rate

$$RR = \frac{v_m * G_{O_2}}{G_{o_2} + k_{m_{o2}}(1 + \frac{G_{co_2}}{k_{mcco_2}})}$$

K_{mO2} = Michaelis constant for O_2 consumption, % O_2

K_{mcco2} = Michaelis constant for competitive inhibition, %CO_2

G = concentration of respective gases, %

2. Uncompetitive

The inhibitor does not react with the enzyme but with the enzyme – substrate complex. Increase in [O2] at high [CO2] has almost no influence on [O2] consumption rate

$$RR = \frac{v_m * G_{O_2}}{k_{mO2} + G_{O_2}(1 + \frac{G_{CO_2}}{k_{muCO2}})}$$

K_{mO2} = Michaelis constant for O_2 consumption, % O_2

K_{muCO2} = Michaelis constant for uncompetitive inhibition, %CO_2

G = concentration of respective gases, %

3. Noncompetitive

Inhibitor reacts with both enzyme and the enzyme substrate complex. [O2] consumption rate in between the above two.

$$RR = \frac{v_m * G_{O_2}}{(k_{m_{O_2}} + G_{O_2})(1 + \frac{G_{O_2}}{k_{mnCO2}})}$$

K_{mO2} = Michaelis constant for O_2 consumption, % O_2

$K_{m\,nco2}$ = Michaelis constant for noncompetitive inhibition, %CO_2

G = concentration of respective gases, %

CO_2 Production during respiration:

Total CO_2 = oxidative + fermentative production rates

V_{CO2} (ox) = RQ * V_{O2}

RQ = respiration quotient,

V = rate of production/consumption of gases, ml/kg h

$$V_{CO_2}(f) = \frac{V_{m_{CO_2}}(f)}{1 + \frac{G_{o_2}}{k_{m_{O_2}}(f)}}$$

v_{mCO2} (f) = max fermentative CO_2 production rate, ml/kg h

k_{mO2} (f) = Michaelis constant for inhibition of fermentative CO_2 production by O_2

Temperature dependence :

- Parameters V_m and K_m are dependent on temperature as described by the Arrhenius law. However, since V_m more strongly dependent on temperature, for sake of simplicity, km may be treated as constants

$$R = R_p * e^{\frac{E_a}{R_{gas}}T}$$

R = model parameter of enzyme kinetics

R_p = pre-exponential factor, T = storage temperature, K

E_a = activation energy, kJ/ g mole

R_{gas} = universal gas constant, 8.314 kJ/ g mole K