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Thermodynamic Properties of Seeds: A Review

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ABSTRACT

Study of isotherms and thermodynamic properties become essential to understand the drying and imbibition mechanisms of seeds. Among post-harvest procedures of seeds, drying is widely known and used in order to assure quality and stability during storage and shelf life. Variation of moisture content through drying is important in order to understand the interaction between water molecules and the seed components, which is the key factor for correct drying and storage. Seed viability could be maintained during long periods owing to their glass structure, as a thermodynamic unstable state, with high viscosity. Thermodynamic properties were enthalpy (Amount of energy available to do work), entropy (Amount of energy present but it not available to do work) and gibbs free energy (Differential energy between the enthalpy and entropy). Thermodynamic properties of seed water determines the reaction kinetics during seed deterioration. Thermodynamic properties showed a critical upper limit, with tolerant species having higher values then susceptible species. In general the values of critical limits of the thermodynamic parameters decreased with increasing temperature. The differential enthalpy and entropy increased in seeds with period of storage and became asymptotic as the seed lost their viability. Thermodynamics properties increased with increase in temperature, indicating that drying and water absorption do not occur spontaneously it requires external energy. A radical drop in germination follows the trend of gibbs free energy increase and enthalpy decrease, indicating intensification of endergonic reaction. Hence, it is concluded that by using thermodynamic properties of seeds the seed quality can be determined without conducting the germination test in shortest period.

Key words: Deterioration, Energy, Germination, Seed drying, Thermodynamics.

Thermodynamics is the branch of bio-physics which deals with the relation between heat and energy. In particularly, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. Thermodynamic properties are the activation energy, enthalpy, entropy and gibbs free energy. Activation energy is the initial energy required by a living systems to initiate or to induce any reactions, whereas enthalpy is the total amount of energy present in system which available to do work. Entropy is the amount of energy present in a system as energy is unavailable to do work, differential between the enthalpy and entropy is known as gibbs free energy is an energy available to do work. In plants thermodynamic reactions takes place in two ways as endergonic and exergonic reactions. Endergonic reaction requires energy to carry out reaction example photosynthesis in plastids and exergonic reaction occurs without any energy requirement at end of the process it provides energy example respiration in mitochondria.

In general all living organisms require thermodynamic changes for its essential biological functions such as growth, respiration, photosynthesis and reproduction. Holzhutter in 2004 reported that the last ten years of 20th century were marked by the application of thermodynamics to research of functional such as *erythrocytes* and reproducible such as *Methylobacterium extorquens* cell growth. In higher plants, seeds contain the functional and reproducible parts connected by the irreversible transfer of hydrolysed monomers from functional (endosperm) to reproducible (embryo). Temperature and moisture play an important role in maintaining and determining the seed quality and its

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capacity of storability. Thermodynamic properties of water content in seed measures the kinetic reaction during seed deterioration (Leopold *et al*., 1994). Thus, the thermodynamic properties of water provide a vision into the cell deterioration mechanism. Thermodynamic has the approaches used to calculate the energy requirements of heat and mass transfer in biological systems and to understand the properties of water (Rizvi and Benado, 1984). Thermodynamic properties of a living tissue are calculated by use of sorption isotherm as suggested by Vertuci and Leopold in 1984 are,

$$\Delta H = \frac{R T_1 T_2}{T_2 - T_1} \ln\left(\frac{a_{w1}}{a_{w2}}\right)$$

$$\Delta G = RT \ln (a_w)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Where,
a_{w1} = Tissue moisture content.
a_{w2} = Relative humidity.
T_1 and T_2 = Lower and higher temperature respectively. ΔH = Enthalpy of hydration.
ΔG = Gibbs free energy.
ΔS = Entropy.
R = Universal gas constant (8.3145 J mol^{-1} K^{-1}).

Thermodynamics of seed and its viability maintenance

A seed is living organism it maintains the viability at anhydrobiosis state for longer period with minimum metabolic process. Anhydrobiosis is a highly stable state in seeds with suspended energy because of very low water content recovery by rehydration. Seeds can maintain their viability for longer period by owning their glassy state which was thermodynamically unstable state (Buitink and Leprince, 2004). At glassy state the viscosity of the tissue is very high it causes the effectively prevented diffusional movement between the tissues. Glass stability in seeds is mainly based on the differential biomolecules linked between hydrogen bonds and water molecules (Walters, 2007). Formation of glassy state (vitrification) in seeds represents the desiccation tolerance capacity and storability (Benson, 2008), whereas vitrification achieves high viscosity without any reorganization in cell organelles (Hatanaka and Sugawara, 2010) and limits the changes in cellular structures (Buitink and Leprince, 2008). Glassy formation is detected by a change in the heat capacity or direct measurement of mechanical relaxation of viscosity (Walters *et al*., 2010).

Moisture content in seeds vary from species to species and also depends on the environment and seed condition, lower moisture content is significant characters of seed (Beardmore *et al*., 2008). Krishnan *et al*. (2004) suggested seed water consists of two types as bound and free water, bound water is moisture present inside the cells cannot be eliminated by drying process if we dry seeds will not able to maintains viability. Free water is present between the cell which is easily removable from seeds, seeds can maintains viability without the free water. Ageing is a characteristic of all living organisms including seeds, regardless to fact that vitrification presents in seeds is a conservation state which is close to anhydrobiosis state, minimum metabolic process with lower ability to neutralise developed injuries.

Pammenter and Berjak (1999) reported that seeds are classified into two groups based upon their ability to maintain their viability during desiccation and storage periods. Orthodox species which could be stored for long periods with extreme desiccation at low temperatures and recalcitrant species could not be stored for long periods which can be dried to lower moisture content because it affected by desiccation injuries during moisture reduction. Correa *et al*. (2016) reported that paddy seeds were dried under different temperatures as 35, 45, 55, 65 and 75°C, activation energy required for initiation of drying process 51.03 KJ mol^{-1}, were as lesser amount of energy is required at high temperature while compared to dry at low temperature. Paddy seeds of two different cultivars *indica* and *japonica* seeds were get equilibrated with salt solution to measure the desorption isotherms, the two cultivars of paddy seeds exhibited two different desorption behaviours one at low moisture content, mechanism of water vapour process was controlled by entropy and the process was controlled by enthalpy at higher temperature (Wang *et al*., 2017).

Thermodynamics of seed deterioration during storage

Water and temperature plays a major role on seed ageing both are interdependent, representing that desiccation is the chief contributor to loss of viability (Beardmore *et al*., 2008). Basic mechanisms in energy transmission during desiccation (Induced by ageing) are redox state (Reduction and oxidation state) of system (Kranner and Birtic, 2005). Shifting of water from the plant tissues through liquid to vapour form as desiccation (Sun, 2002). Energy status of moisture in plant tissue and humidity pressure in air at both dry and hydrated stage is influenced by the temperature. As environmental temperature increases the equilibrium moisture content in living tissue is get decreased as vice versa. During seed ageing disturbance of glassy structure is due to structural changes by seed deterioration (Hoekstra *et al*., 2001) and it leads to increased oxidative activity (Dussert *et al*., 2006) results higher respiration rate. The changes of internal energy of a system represents maximum work which could be achieved observed based on the thermodynamics.

Respiration rate of dry seeds are influenced by the both internal as glassy state and external as temperature levels (Walters *et al*., 2001). Krishnan *et al*. (2004), stated that thermodynamic properties of seed moisture decides the reaction kinetics during seed deterioration. Among the orthodox and recalcitrant species the thermodynamic properties are higher in tolerant species compare to susceptible species. While increases in temperature the thermodynamic parameters are get reduced. Dragicevic (2007), reported that increased values of differential free energy find during accelerated ageing of susceptible sugary genotype and tolerant dent genotypes of maize seed. Increases in gibbs free energy values indicates intensification of endergonic reaction and consumption of relatively high amounts of energy (Davies, 1961). Krishanan *et al.* (2004), suggested that relation between seed deterioration dependence of the thermodynamic properties of seed moisture namely water potential, water activity, differential enthalpy, entropy and free energy were examined in two different seed species sensitive soy bean, tolerant wheat, differing in their sensitivity to storage under accelerated ageing condition. Seed deterioration was compared with germination percentage, seed leachate, conductivity and the various thermodynamic parameters seed water indicated that seed germination decreased faster at 45°C then at 35°C. In both the crop seeds differential enthalpy and entropy with increased storage period and became close to their viability loss. Loss of seed viability and raised seed leachates shows that changes in thermodynamic properties of seed moisture reflect on the seed deterioration during accelerated ageing.

Panayotov and Aladjadjiyan (2014), reported that the pepper seeds were stored under ambient condition for 132 months, seed viability and seed germination were measured at yearly intervals, seed viability was maintained upto 4-5 years at 70 per cent germination after that seed viability was get reduced, with relation to thermodynamic properties as entropy, enthalpy and gibbs free energy get reduced same as also observed in the seed viability. From this we can also measure the seed quality through the thermodynamic parameters. Thermodynamic parameters corresponding to the start of seed deterioration during storage can be identified as the critical upper limit for the parameter for seed storage at particular temperature (Krishnan *et al*., 2004).

Thermodynamics of seed germination

The introduction of thermodynamic parameters could enable a better understanding of the process of growth and reactions, as hydrolysis and biosynthesis during seed germination. Boyer in 1969, quantified the water transport into plant based on the energy concept. In Smith *et al*. (2006) reported that thermodynamic model to describe relation between plant growth and respiration rates. When considered together simultaneously measured values of carbon di oxide production rate, oxygen use rate and metabolic heat rate provide a link between cellular and whole plant process. 25 KJ mol^{-1} is taken as total enthalpy change per mole of carbon incorporated into biomass. The rapid intake of water during imbibition by the laws of thermodynamic diffusion and osmosis, present during phase I of imbibition is followed by enthalpy domination and an increase of free energy status increased during phase II of imbibition (Sun, 2002). The energy required for activation of a process is provided by temperature of the environment, the energy of the double phases shifting of water front (Osborne *et al*., 2002). Energy required for biochemical reactions preceding germination process is produced by intensive respiration, activated during first hours of imbibition (Sanchez-Nieto *et al*., 2011). A high negative enthalpy value at low water content suggests the strong affinity of water molecules to polar sites. The lack of measurable respiration at moisture contents less than 8% is consist with the lack of activity for most enzymes at such dry condition. The region ranges from 8 to 25% moisture has been termed the region of restricted metabolism. This is range in which liquid water first appears and the differential entropy values indicate first solution effects. The primary hydration process is considered to be completed when the differential enthalpy of hydration approach zero.

On viable seeds Krishnan *et al*. (2004), established that germinating and non-germinating seeds consist of three types of moisture as bound, bulk and free moisture in phase I of imbibition. Bulk moisture disappeared completely in non-germinating seeds during II phase of imbibition. Whereas in germinating seeds three types of moisture were observed during II phase of imbibition. The moisture front brings energy into seed, contributing to an increase in the thermal energy necessary for the commencement of activation energy. In imbibed seeds the biochemical reaction attains a critical point, inducing cell division, initiation of germination which results of new plant from embryo. Although living systems are non-linear thermodynamic systems are far removed from equilibrium (Trepagnier *et al*., 2004), it is necessary to hypothetically defined an energy balance for partial phases and processes. According to Hess Law, free energy is cumulative, irrespective of its origin, hence all potential energy presents in a plant system is given by the sum of the individual energy states, resulting from the double phase shifting of water and that released from all the hydrolysis and biosynthesis reactions. During imbibition release of leachates from seeds indicates that the permanent loss of energy. Sredojevic *et al*. (2008), reported that free energy loss due to leaching process alone for soy bean and sunflower as 36% and 46% respectively between 1^{st} and 8^{th} day of the germination process.

CONCLUSION

Plants to maintain structure with the minimal expenditure of energy, they are able to conserve energy in substances they form structures with stored energy to supress negative conditions and to increase their reproduction ability. A seed is biological system in a vitrified state. At vitrification state for seed conservation with silent metabolic process lower abilities to counter developed injuries. The differential enthalpy and entropy increases in seeds with storage time and seed get close to lose their viability. The germination process requires energy, which is provided by environmental temperature and double shifting of water front. Thermodynamic properties increased with increase in temperature, indicating that drying and imbibition does not occur spontaneously it requires external energy. During drying at lower temperature it requires higher thermodynamic energy to initiate the process and also longer time to finish, at higher temperature it requires lower energy and time consumed. In general, the thermodynamic parameters showed a rapid increase before the onset of seed deterioration, which indicates that the loss of seed viability. Hence, thermodynamic properties of seed moisture and temperature combinations are the better parameters for assessing seed deterioration. During seed storage decreases in thermodynamic parameters correlated with decrease in seed germination. Hence, conclude that the thermodynamic properties of seeds are one of the alternative parameters to determine the seed quality without going for germination test and through this we can assess seed quality at shortest time, when the thermodynamic properties and germinability of seeds were correlated.

Conflict of interest: None.

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