

Challenges beyond F-Value, Water Activity and Glass Transition Concept in Determining Food Stability

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Abstract

Theoretical concepts of F-value, water activity and glass transition are the most successful in determining food stability during food processing and storage. The water activity and glass transition concepts are progressed by combining these concepts in a stability map named as state diagram. The first part of this paper provides stability criteria based on F-value, water activity, glass transition and state diagram. The second part explains the recently proposed macro-micro region concept in the state diagram. In this concept, 13 micro-regions are mapped and then relative stability criteria between the micro-regions are postulated. Final part presents real challenges in combing different hurdles in food preservation.

1. Introduction

It is a challenge to the food scientists and engineers to determine food stability from a scientific basis rather than empiricism. The modern food processing developed at the end of the 1700s when the Napoleonic wars raged. As Napoleon pushed forward into Russia, his army was suffering more casualties from scurvy, malnutrition, and starvation. The French government offered 12,000 francs to anyone who could develop a method of preserving food. In 1795 Nicolas Appert, a chef took up the challenge. He had a theory that if fresh foods were put in airtight containers and sufficient heat applied, and then the food would last longer. Appert packed foods in bottles, corked them, and submerged them in boiling water, thus preserving them without understanding of bacterial spoilage. After 14 years of experimentation, in 1809 he won the prize and this was given to him by Napoleon himself¹. In 1804 France military had opened their first vacuum-packing plant. Although the process was a French military secret, it soon leaked across the English Channel². In 1810, an Englishman, Peter Durand, took the process a step further and developed a method of sealing food into unbreakable tin containers. This technique was perfected by Bryan Dorkin and John Hall, who set up the first commercial canning factory in England in 1813³.

A theoretical understanding of the benefits of canning did not come until Louis Pasteur observed the relationships between microorganisms and food spoilage after fifty years later. By the 1860s the time required to process food in can was reduced from 6 hours to 30 min through numbers of inventions and improvements. The sterilization of canned foods has a long tradition and it is most likely that it will continue to be popular because of its convenience and extended shelf-life (1-4 years at ambient temperature) and for

being economic³. The time of sterilization process is estimated based on F-value concept.

In the 1950s scientists began to discover the existence of a relationship between the water contained in a food and its relative tendency to spoil. W. J. Scott, an Australian scientist, proposed that the active water could be much more important to the stability of a food than the total amount of water present. The legacy of Scott allowed scientist to develop generalized rules or limits for the stability of foods using water activity⁴. Labuza et al.⁵ proposed the earlier food stability maps based on the water activity concepts containing growth of micro-organisms and different types of bio-chemical reactions. Recently, an updated stability map was presented by Rahman¹.

Scientists identified numbers of limitations of the water activity concepts and glass transition concepts in the literature. Glassy materials have been known for centuries but the glass transition concept was first applied to foods with scientific understanding in the 1980s⁶. The glass transition concept postulated that foods are most stable at its glassy state (i.e. below glass transition temperature). White and Cakebread⁷ first highlighted the importance of the glassy state of foods in determining its structural stability. They were perhaps the first food scientists to discuss the importance of the glassy and rubbery states in relation to the collapse of a number of high solid systems. The significant applications of the glass transition concept emerged in food processing in the 1980s, when Levine and Slade⁸ and Slade and Levine⁹ identified its major merits and wide applications.

The glass transition concept was further advanced by developing a state diagram for foods. A state diagram is a stability map of different states and phases of a food as a function of water or solids content and temperature¹⁰. Most probably Levine and Slade⁸

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presented the first state diagram of providone N-vinyl pyrrolidone (PVP) in the food science literature by illustrating glass line, freezing curve, and intersection of these lines as T_g'' by extrapolation of the extended freezing curve by maintaining similar curvature. The main advantages of drawing a map are to help understanding the complex changes when the water content and temperature of foods are changed. It also assists in identifying stability of foods during storage as well as selecting a suitable condition of temperature and moisture content for processing. This state diagram provided four macro-regions. In the literature it was emphasized that a combination of water activity and glass transition concepts could be a powerful tool in predicting water activity. These approaches to combine both concepts are reviewed by Rahman^{11,12}. Rahman¹³ combined glass transition and water activity concepts in the state diagram by plotting BET-monolayer values as a function of temperature.

A macro-micro region concept combining water activity and glass transition concepts in the state diagram was first presented in the 18th International Congress of Chemical and Process Engineering (CHISA 2008), 24-28 August 2008, Prague, Czech Republic, and was subsequently published in the International Journal of Food Properties¹. Based on this, Rahman¹ developed the state diagram and hypothesized 13 micro-regions having the highest to the lowest stability based on the location from glass transition and BET-monolayer lines. In the literature, water mobility and critical temperature concepts are also proposed to determine the food stability. The objective of this review is to explain the concepts of water activity, glass transition, state diagram, and macro-micro region in determining food stability.

2. F-Value

The inactivation target in sterilization process in canned products depends on the types of heat resistance bacteria and pH of foods. It is possible to classify food products into three groups according to pH: low-acid (pH \geq 4.6), medium-acid (3.7 \leq pH \leq 4.6), and acid foods (pH \leq 3.7). The target microorganism in the thermal processing of low-acid food (pH \geq 4.6) is *Clostridium botulinum*. The processing time based on first order kinetics can be estimated as^{14,15}:

$$t = -\frac{1}{k} \ln\left(\frac{N_F}{N_o}\right) = \left(\frac{D}{2.303}\right) \ln\left(\frac{N_o}{N_F}\right) \quad (1)$$

Where, k is the destruction rate constant (s^{-1}), N_o and N_F are the initial and final numbers or concentrations of micro-organism, and D is the decimal reduction time (s), respectively.

The above equation indicates that final concentration tends to zero when time tends to infinity, thus it would not be possible practically to reach a final concentration of zero for the target micro-organism. Considering this point, the commercial sterilization criterion should be defined so that it is possible to design a process that is safe but occurs within a finite time and which is economically and practically feasible³. According to Stumbo¹⁶, commercial sterilization criterion was established arbitrarily.

The commercial sterilization criterion states that the minimum thermal process should reduce initial micro-organism concentration by 10^{12} . This is well known as 12D concept or "botulinum cook". The commercial sterilization was used for several reasons: (i) to determine safety margins, (ii) to determine cooking requirements, and (iii) to prevent the growth of thermophilic spoilage microorganisms. The probability argument says, in 12D treatment there will be one spore in 10^{12} cans¹⁵. Considering 100 million cans consumed per day, an estimate over a 100-year period worldwide consumption will be 3.65×10^{12} cans and the 12D criterion would predict three to four outbreaks every 100 years³.

If we know D_T value of target micro-organism at the temperature T , we can estimate the processing time to achieve 12D. However, the processing time varies with the size of a can. Considering $D_{121.1} = 0.21$ min for *C. botulinum*, one spore per g and can size of 0.1 L (density: 1 g/cc), the processing time (t) to achieve 12D is 2.94 min from Eq. 1³. Similarly if the can size is 5 L, the processing time is 3.29 min. Since any thermal process could not be performed at a specific temperature instead a varied temperature range during heating and cooling time, thermal death time F_o is defined for processing as:

$$F_o = \int_0^t 10^{\frac{T-T_r}{z}} dt \quad (2)$$

Where F_o is the processing time (s), F_r is the death time at a reference temperature, T_r is the reference temperature and z is the thermal resistance constant or z-value. Currently, a common commercial sterilization treatment for *C. botulinum*, F_o is in the range of 6-8 min, although some companies use F_o of 10 min or higher. Considering this processing time, 5L can size and the minimum time requirement (6 min) at 121.1°C, indicated 1.335×10^{-25} spores per package. Applying the probability concept, we should expect one outbreak in several billion years (to be precise, one hundred thousand billion years). In fact, at least in the past 50 years no outbreak has been directly related to the sterilization criterion³.

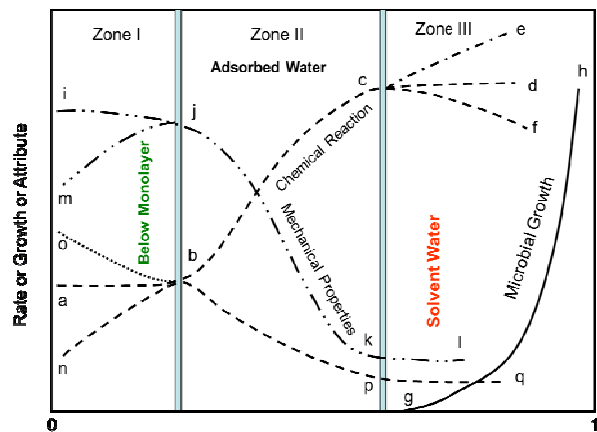


Fig. 1. Stability diagram based on the water activity concepts. gh: microbial growth trend; ob, ab, nb: chemical reaction trends below BET-monolayer; bc, bp: chemical reaction trends in the adsorbed water; ce, cd, cf, pq: chemical reaction trends in the solvent water region; ij, mj: mechanical properties trends below BET-monolayer; jk: mechanical properties trend in the adsorbed water region; kl: mechanical properties trend in the solvent water region (Rahman, 2009)

3. Water Activity Concept

Water activity indicates the state of water in foods. In general the rules of water activity concept are: (i) food products are most stable at their ‘BET-monolayer’ content or ‘BET-monolayer water activity’ and unstable above or below BET-monolayer; (ii) there are a critical water activity limit for a specific micro-organism or a class of micro-organism for their growth or toxin production, and biochemical reactions^{5,17-21}. In the current food stability map, Rahman¹ presented the trends of microbial growth, bio-chemical reactions and mechanical characteristics are presented in the three zones of water activity (Fig. 1). In fact, the BET-monolayer could be only achieved in the cases of dried foods. This water activity map provides the different dynamics for chemical reactions. For examples, below monolayer (zone I): (i) stability can be decreased with increasing water activity, for example fat oxidation (line ob); (ii) stability can remain constant (line ab); and (iii) stability can increase (line nb). In the adsorbed layer (zone II): (i) stability can increase (line bp); and (ii) stability can decrease (line bc). In multi layers (zone III): stability can increase, decrease or remained constant. The limitations of the water activity concepts are thoroughly reviewed by Rahman¹.

4. Glass Transition Concept

Considering the limitations of water activity concept, the hypothesis of glass transition concept was put forward. Glassy materials show two major

characteristics: inert (i.e. low molecular mobility), and brittle. The rules of the glass transition concept are: (i) the food is most stable at and below its glass transition (i.e. T_g or T_g'), and (ii) the higher the $T-T_g$ or T/T_g (i.e. above glass transition), the higher the deterioration or reaction rates^{9,22,23}. It is clear from the literature that all experimental results could not be explained by the above rules^{1,13}, thus further developments are necessary. The limitations of water activity and glass transition concepts would not invalidate the concepts completely rather make it difficult to apply universally. The water activity concept is based on the binding nature of water molecules in the matrix. When water is bound (i.e. unavailable to take part in reactions) to the solid matrix or non-solvent, then no deterioration reactions could be expected. The glass transition concept is based on the molecular mobility of the reacting components at micro-level in the matrix, thus diffusion of the reactants through the system to take part in reaction is very slow and stability is achieved. Thus a successful combination of water activity and glass transition could open more precise and unified determination of stability criteria. There should be a break (i.e. change in the slope between above and below the critical ratio) in the plot at T/T_g equal to 1 if glass transition concept is valid or X_w/X_b equal to 1 if water activity concept is valid. Considering the fact that glass transition is not the critical limit, Rahman¹¹ tested the hypothesis that there is a critical temperature as a ratio of T_c/T_g , which could vary with moisture content. Above the critical temperature, an increase in the water content or temperature significantly increased the reaction rate while below the critical temperature the rate was relatively less affected by water content and temperature. He observed values of T_c/T_g varied from 0.78 to 1.5 depending on the types of reaction and the matrices. In some instances, the values of T_c/T_g were close to 1.0 indicating only glass transition could explain the process. Moreover the deviations of T_c/T_g from 1 explained why in many instances in the literature both stability and un-stability was observed above and below glass transition.

5. State Diagram

The state diagram based of freezing curve and glass transition provided four macro-regions: region I (i.e. below glass transition), region II (above glass transition and below maximal-freeze-concentration, i.e. completely frozen), region III (above maximal-freeze-concentration condition and below freezing curve, i.e. partially frozen), and region IV (i.e. above glass transition and above freezing curve)^{8,9,13}. Rahman¹³ combine water activity and glass transition concepts in the state diagram by plotting BET monolayer as a function of temperature. This makes four regions: below BET-monolayer, one above and one below; and above BET-monolayer, one above and another below.

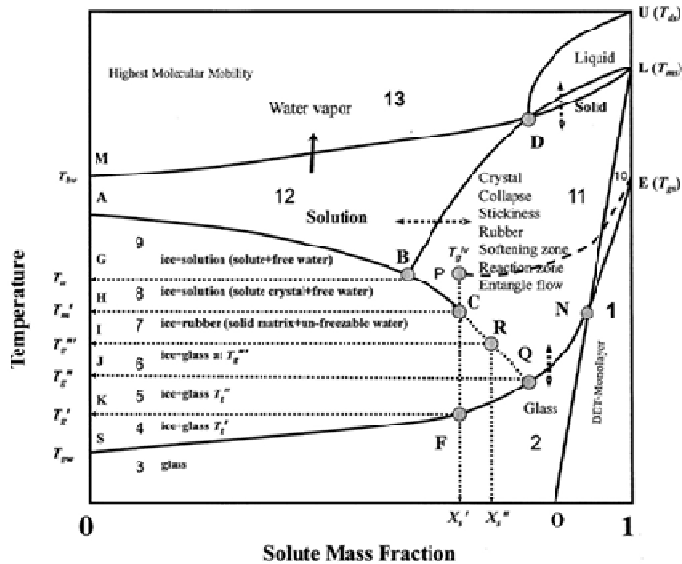


Fig. 2. State diagram showing different regions and state of foods, 1-13 indicate the micro-regions (updated from Rahman, 2006; Rahman, 2009)

6. Macro-Micro Region Concept

Rahman¹ developed the state diagram as shown in Fig. 2 and hypothesized 13 micro-regions having the highest to the lowest stability based on the location from the glass transition and BET-monolayer lines. For example, region-1 (relatively non-reacting zone, below the BET-monolayer line and glass line) is the most stable and region-13 (highly reacting zone, far from BET-monolayer line and glass line) is the least stable. The stability decreased as the zone number increased. The most unstable micro-region is the region 13 since it is the most reactive mobile region. Applications of this concept in food processing are presented by Rahman^{12,13}.

7. Future Needs and Concluding Comments

The water activity, glass transition or state diagram is the simplified nature of the real complexity. It would be interesting to incorporate other concepts in order to provide a more complete picture of food stability. The glass transition by thermal or mechanical relaxations measures mobility in a 20-300 nm range, while other relaxation techniques, such as Nuclear Magnetic Resonance (NMR) measures the molecular relaxation in a 1-2 nm range²⁴. There are number of attempts are being made to relate glass transition and other mobility. However, generic trends or universal rules were unable to establish. All foods are not at BET-monolayer or below glass transition, thus other hurdles play roles in many foods. At present nearly more than 60 hurdles may involve in food preservation²⁵. In combining

several hurdles, such as water activity, storage temperature, F_o value and pH into an unified theoretical foundation is a real challenge to the food scientists and engineering.

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