



Enthalpy-Entropy Compensation in the Gelatinization of *Cyperus* Starch

Cyperus Nişastasının Jelatinizasyonunda Entalpi-Entropi Kompensasyonu

✉ Jonghoon KANG^{1*}, ✉ Luz GREEN², ✉ Kwajalen HALL³

¹Department of Biology, Valdosta State University, Valdosta, Georgia, USA

²Department of Psychology, Valdosta State University, Valdosta, Georgia, USA

³Department of Chemistry, Valdosta State University, Valdosta, Georgia, USA

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Dear Editor,

A recent paper by Olayemi et al.¹ examined various properties of starch cross-linked with citric acid to improve its physicochemical characteristics. This modified starch has considerable applications in food and pharmaceutical industries. The citric acid used in the study was derived from fruit wastes (orange peels)-an approach followed in green chemistry. We agree with the authors that the green chemistry approach is valuable from an environmental perspective because of the various benefits it confers, such as safe operability, faster processing, easy scalability, and less energy consumption.²

Of the physicochemical characteristics of starch, the authors measured the thermodynamic parameters of gelatinization. These parameters are used to examine the effects of sampling time point of the liquid substrates of orange peels, which served as a source of citric acid for starch modification. The authors prepared four types of starch: TS0, TS1, TS2, and TS3. TS0 is native starch without any cross-linking, whereas TS1, TS2, and TS3 are starch types cross-linked with citric acid in the liquid substrates of orange peels, which were produced by natural solid-state fermentation on day 5, 10, and 15, respectively. The authors performed differential scanning calorimetry to characterize the gelatinization of the four sets of starch in terms of thermodynamics. They measured enthalpy (ΔH) and

three characteristic temperatures, onset, peak, and conclusion, of gelatinization.

On the basis of their data, the value of ΔH was positive for all four samples, indicating that starch gelatinization is an endergonic process. Although ΔH provides valuable information about starch gelatinization, another major thermodynamic parameter, entropy (ΔS), was not discussed in their paper. In this letter, we present our analysis of their results to provide the numerical values of ΔS in the gelatinization of various types of starch.

Starch gelatinization is a type of phase transition,³ and ΔS in a phase transition can be determined by the following equation:⁴

$$\Delta S = \frac{\Delta H}{T_m} \quad \text{equation (1)}$$

Where T_m is the melting temperature, the mid-point temperature in phase transition.³ Although information about T_m was not available in the original paper, the peak temperature in starch gelatinization was found to be in considerable agreement with T_m .³ Therefore, we used the peak temperature reported in the original paper as a substitute for T_m in our analysis. Using the numerical values of ΔH and the peak temperature in the gelatinization of the four types of starch in equation (1), we obtained ΔS for each type.

*Correspondence: jkang@valdosta.edu, Phone: 1-229-333-7140, ORCID-ID: orcid.org/0000-0001-5594-6141

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Figure 1 shows the resulting values of ΔS and ΔH for each type of starch. The graph clearly illustrates two features of starch gelatinization. First, both native and cross-linked types of starch had positive values of ΔS . This implies that starch gelatinization is an entropy-driven process ($\Delta S > 0$), regardless of the modification status. Second, ΔH exhibited a wide variation among the starch types. For instance, the difference of ΔH between TS1 and TS2 was >1500 J/g; however, the difference in their peak temperature was $<20^\circ\text{C}$. This is a consequence of the compensatory behavior between enthalpy and entropy, which is referred to as enthalpy-entropy compensation.⁵ Linear regression identified a numerical relationship between enthalpy and entropy (R^2 : 0.9982):

$$\Delta S = \alpha \times \Delta H + \beta \quad \text{equation (2)}$$

Where the values of α and β and their standard errors were $2.4 \times 10^{-3} \pm 7.3 \times 10^{-5}$ and $4.7 \times 10^{-2} \pm 0.11$, respectively.

This phenomenon has been observed in various weakly coupled systems such as the melting of human hair, which is made of keratin proteins.⁵ Our analysis elucidated that modification of starch through cross-linking with citric acid can result in a significant variation in both ΔH and ΔS in gelatinization (Figure 1). However, owing to the enthalpy-entropy compensation, the variation in the peak temperature was highly limited to 17°C !

Another feature evident in the results of the original paper¹ is the inconsistency between the duration of fermentation of orange peels and the thermodynamic parameters (Figure 2). Although the authors proposed a plausible mechanism for the inconsistency, it clearly demonstrated a unique feature of green chemistry: minimum human intervention on a system results in unpredictable fluctuations in the physical and chemical variables of the system. One of the chemical variables of the orange peel substrates examined in the original paper¹ was the pH of the orange peel liquid substrates. Although the pH itself

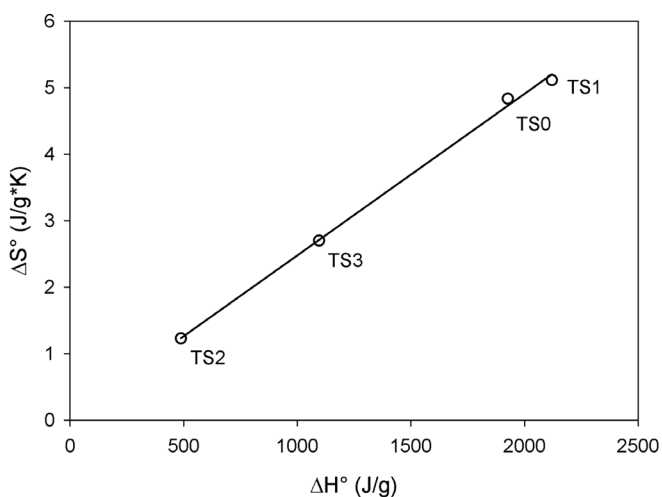


Figure 1. Enthalpy-entropy compensation in starch gelatinization. Solid line is a plot of equation (2). Linear regression was performed using SigmaPlot (Systat Software, San Jose, CA)

was inconsistent with fermentation duration (Figure 2), we recognized a significant correlation between the thermodynamic parameters of gelatinization and pH (Figure 3) as the R^2 value in both cases was 0.9951. The correlation of enthalpy and entropy with pH is shown in equations (3) and (4), respectively:

$$\Delta H = a_1 \exp(-b_1 \times \text{pH}) \quad \text{equation (3)}$$

$$\Delta S = a_2 \exp(-b_2 \times \text{pH}) \quad \text{equation (4)}$$

Where $a_1 = 11.6 \times 10^4 \pm 4.6 \times 10^4$, $b_1 = 2.0 \pm 0.2$, $a_2 = 243.9 \pm 92.5$, and $b_2 = 1.9 \pm 0.2$. Equations (3) and (4) together elucidate a mathematical reason for the enthalpy-entropy compensation in starch gelatinization (Figure 1). Normalized enthalpy and entropy showed a similar pH dependency: The decreasing factors were 2 and 1.9 for enthalpy and entropy, respectively. The t-test indicated that the difference between b_1 and b_2

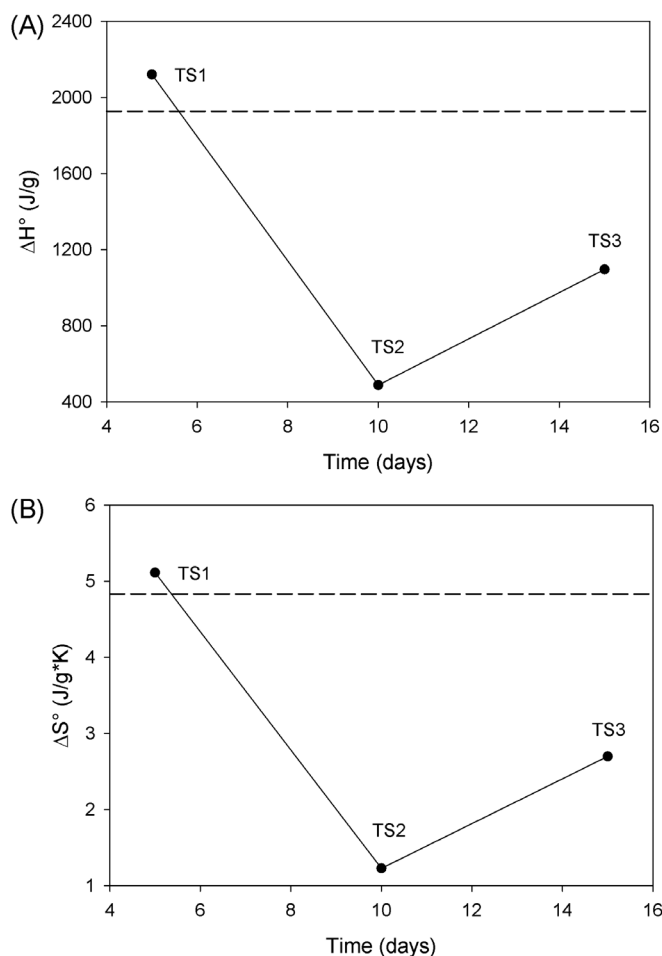


Figure 2. Correlation of enthalpy (A) and entropy (B) with time. The correlation coefficient between enthalpy and time was -0.621 ($p=0.573$) and between entropy and time was -0.615 ($p=0.578$). In both cases, no correlation was noted between any pairs of the parameters shown in the figures as p was >0.05 . The dashed line in each plot represents the corresponding value of the native starch (TS0)

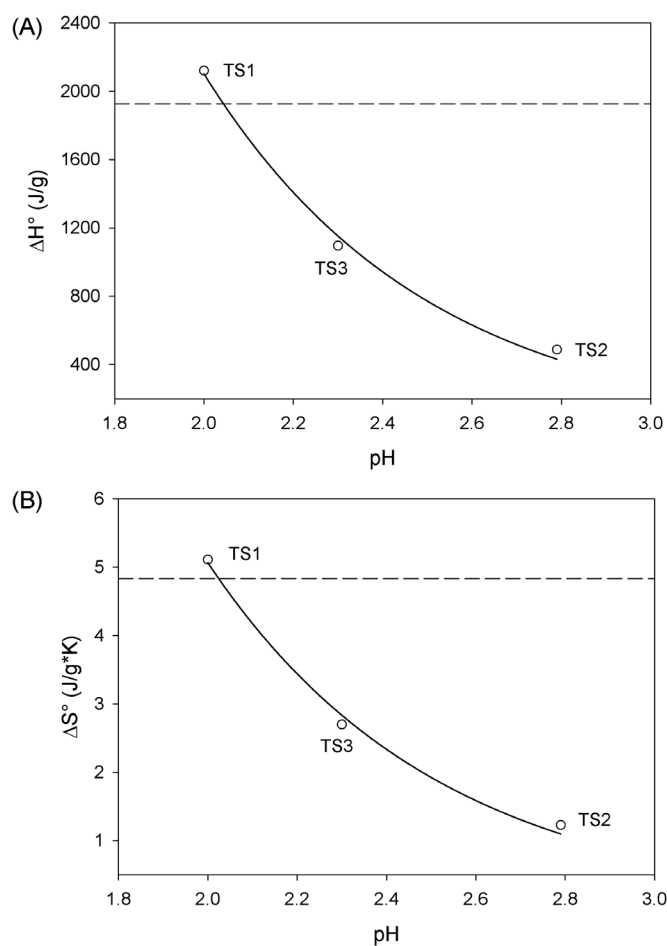


Figure 3. Correlation of pH with enthalpy (A) and entropy (B). Solid lines are the best fits of each case: Equation (3) in (A) and equation (4) in (B). The dashed line in each plot represents the value of the native starch (TS0)

was not statistically significant ($t: 0.254$, $df: 2$, $p=0.823$), strongly suggesting that enthalpy and entropy have a similar pH dependency. This numerical similarity is responsible for

the high degree of correlation between enthalpy and entropy (Figure 1).

In conclusion, cross-linking of starch with citric acid at various pH values shows an enthalpy-entropy compensation. This compensation may be attributed to the similar quantitative relationship of pH with enthalpy and entropy. Finally, we would like to correct an error in the original paper that the unit of enthalpy of gelatinization is J/g and not J/g·K.

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