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Thermodynamic properties of vitamin C thermal degradation in wedang jeruk

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Abstract. Wedang jeruk is one of Indonesia's special drinks. Wedang jeruk can be made from citrus, tea, and sugar. The purpose of this study was to determine thermodynamic properties of thermal degradation of vitamin C in wedang jeruk. Thermal degradation was carried out at 313-353 K for 90 minutes. The result shows that the enthalpy of activation ranged from 12.82 kJ/mol to 38.47 kJ/mol while entropy ranged from -0.31 kJ/molK to -0.23 kJ/molK. The enthalpy of activation indicates that degradation of vitamin C is endothermic processes. The value of enthalpy and entropy indicates the value of Gibbs-free energy is positive which means the reaction goes non-spontaneously. The harmonic temperature is higher than the isokinetic temperature. This reaction driven by entropy.
Keywords: thermodynamic, thermal degradation, vitamin C

1. Introduction

Wedang jeruk is a special drink from Indonesia. It can be made from citrus water with the addition of water and sugar [1]. In general, wedang jeruk is served hot. Wedang jeruk is high in vitamin C content. Vitamin C is damaged easily by heat [2, 3]. As a modification, wedang jeruk can be added with tea, ginger or cinnamon. The interaction between the citrus water, sugar, tea, ginger, and cinnamon lead to changes in thermal degradation kinetics of vitamin C.

Kinetics changes can affect the thermodynamics of thermal degradation on vitamin C content. The kinetics of Vitamin C degradation cause by heat have been investigated by a lot of authors [4-6], however there has been relatively little work on thermodynamics properties during this process. Thermodynamics of degradation is an important area of interest for food engineering. Thermodynamics is applied in several engineering operations such as heating, evaporation, refrigeration, and mass transfer operations [7].

The theory that widely used to study the phenomenon of physical and chemical changes in food is the enthalpy-entropy compensation theory. This theory states that compensation arises from changes in the interaction between the solute and the solvent that causes the reaction [8]. This theory also says that the relationship between enthalpy and entropy for specific reactions is linear [9]. Rudra *et al.* [10] used the enthalpy-entropy compensation theory to study reaction during thermal degradation of Chlorophyll in mint and coriander puree. Pascual-Pineda *et al.* [11] used the enthalpy-entropy compensation theory to study the stability of paprika nanoemulsions. According to the enthalpy–entropy compensation, the carotenoid red fraction was enthalpy driven, whereas the carotenoid yellow fraction was entropy controlled.

The purpose of this study was to determine thermodynamic properties of thermal degradation of wedang jeruk using enthalpy-entropy compensation theory. From the enthalpy-entropy compensation we can choose the environment to inhibit undesired reaction or enhance desired reaction.

2. Materials and Methods

2.1. Wedang Jeruk Preparation
Citruses, tea, and sugar were obtained from the local market in Salatiga. The citruses were washed and squeezed (part A). 5 grams of tea and 25 grams of sugar were boiled with 300 mL of water (part B). 0 mL of part A was mixed with 280 mL of part B after it was cooled.

2.2. Kinetics data analysis
The mixture was heated in the water bath (40°C, 60°C, and 80°C) for 90 minutes. Vitamin C determination was done every 15 minutes. Vitamin C determination was done based on the iodometric method. It has been established by several researchers that the thermal degradation of vitamin C follows the first order rate kinetics model [4-6]. Integrated form of the first order rate kinetics model is:

$$\ln C - \ln C_0 = -k_i t \quad (1)$$

where C is the measured vitamin C (ppm); C_0 is the initial vitamin C content of the wedang jeruk; t is the heating time (min); k_i is the rate constant for vitamin C degradation (ppm/min).

2.3. Thermodynamic parameter ($\Delta H^{\#}, \Delta S^{\#}, \Delta G^{0\#}$) estimation [10]
According to the Eyring equation of activated complex theory, rate reaction constant can be written as:

$$k_i = \kappa \times \frac{k_S \times T}{h} \times K^{\#} \quad (2)$$

where κ is transmission factor (dimensionless), k_s is Boltzmann constant (1.38×10^{-23} JK^{-1}), h is Plank's constant (6.63×10^{-34} Js) and $K^{\#}$ is the equilibrium constant of the activation complex (dimensionless). On the other side the standard state Gibbs free energy of activation can be written as:

$$\Delta G^{0\#} = -RT \ln(K^{\#}) \text{ or } K^{\#} = e^{-\Delta G^{0\#}/RT} \quad (3)$$

Combining equation 2 and 3, the following equation was obtained:

$$k_i = \kappa \times \frac{k_S \times T}{h} \times e^{-\Delta G^{0\#}/RT} \quad (4)$$

Standard state Gibbs free energy of activation has relationship with enthalpy and entropy and can be written as:

$$\Delta G^{0\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (5)$$

Combining equation 4 and 5, the following equation was obtained:

$$\ln\left(\frac{k_i}{T}\right) = \left[\ln\left(\frac{k_S}{h}\right) + \left(\frac{\Delta S^{\#}}{R}\right)\right] - \left[\left(\frac{\Delta H^{\#}}{R}\right)\left(\frac{1}{T}\right)\right] \quad (6)$$

From equation (6) we can determine $\Delta H^{\#}, \Delta S^{\#}$, and $\Delta G^{0\#}$ by regression of ln $\frac{k_i}{T}$ vs. $\frac{1}{T}$

2.4. Compensation theory [11]
The relationship between enthalpy and entropy of activation can be written as:

$$\Delta H^{\#}{}_T = T_B \Delta S^{\#}{}_T + \Delta G^{\#}{}_B \quad (7)$$

where T_B is isokinetic temperature (K) and $\Delta G^{\#}{}_B$ is the measure of the free energy at T_B (J/mol). Isokinetic temperature represents the temperature which all reaction in the series proceed at the same rate.

The mayor factor driven the mechanism can be determined by compare isokinetic temperature and harmonic temperature (harmonic mean of the experimental temperatures). The harmonic temperature was defined as:

$$T_{hm} = \frac{N}{\sum_{i=1}^{N}\left(\frac{1}{T}\right)} \quad (8)$$

where N is the total number of temperatures. If $T_B > T_{hm}$ the process is enthalpy driven, while if the opposite condition is observed ($T_B < T_{hm}$), the process is considered to be entropy-controlled [12].

3. Results and Discussion

Equation (1) is used to determine the value of the reaction rate constant. R^2 values are used to determine whether the reaction runs according to first order. Table 1 shows the value of the reaction rate constant and R^2. Table 1 shows that the reaction follows first order. This result is in accordance with previous research [4-6]. Wedang jeruk with sugar addition has the lowest reaction rate constant. The earlier study on the kinetics of vitamin C degradation in fresh strawberry juice shows the same result [13]. The vitamin C loss was decrease upon sugar addition. The phenomenon implies that the degradation rate of vitamin C could be retarded simply by addition of sugar. This seemed plausible that the sugar presence would decrease the concentration of dissolved oxygen in the juice, thus the oxidation process of vitamin C was delayed. It has been reported that sucrose was able to inhibit vitamin C oxidation in a closed aqueous system [14].

Table 1. Reaction rate constant, R^2 and MRD for vitamin C degradation in thermally processed wedang jeruk.

Additives	Temperature (K)	k_i	R^2
No additives	313	$3x10^{-4}$	0.9940
	333	$3x10^{-4}$	0.9663
	353	$6x10^{-4}$	0.9844
Tea	313	$8x10^{-5}$	0.7070
	333	$2x10^{-4}$	0.9813
	353	$2x10^{-4}$	0.8952
Sugar	313	$6x10^{-5}$	0.9818
	333	$7x10^{-5}$	0.9777
	353	$8x10^{-5}$	0.9534
Tea and Sugar	313	$1x10^{-4}$	0.9859
	333	$2x10^{-4}$	0.9115
	353	$4x10^{-4}$	0.6275

k_i: reaction rate constant (min^{-1})

The enthalpy and entropy values of activation computed using equation (6) are reported in table 2. The calculation starts by plotting ln $\frac{k_i}{T}$ vs. $\frac{1}{T}$. the slope and the intercept of each plot converted into enthalpy and entropy values of activation based on equation (6). The enthalpy of activation for vitamin C degradation in wedang jeruk ranged from 3.85 to 29.04 kJ/mol with addition of sugar has the lowest value of enthalpy of activation and addition of tea and sugar has the highest value of enthalpy of activation. The values of enthalpy show an endothermic state between activated complex and reactant which leads to increase of the degradation with increasing temperature [15]. The entropy of activation for vitamin C degradation in wedang jeruk ranged from -0.31 to -0.23 kJ/mol with addition of sugar has the lowest value of enthalpy of activation and addition of tea and sugar has the highest value of enthalpy of activation. The higher value of entropy with addition of tea and sugar in contrast to other additive attributed to relatively less ordered state in high concentration wedang jeruk, due to an increase in the number of molecules [15]. The negative values of entropy indicating that the transition state has less structural freedom than the reactant [16]. The positive value of enthalpy and negative value of entropy is a common value for thermal reaction [10, 11, 15].

The Gibbs free energy is defined as the difference between energies of reactants and activated state and is usually served as a measure of process spontaneity [15]. Positive ΔG values indicated that vitamin C thermal degradation is non-spontaneous reaction.

Table 2. Enthalpy and entropy* of activation for vitamin C degradation in wedang jeruk.

Additives	Temperature (K)	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (kJ/molK)	$\Delta G^{0\#}$ (kJ/mol)
No additives	313	12.82	-0.27	97.33
	333			102.73
	353			108.13
Tea	313	18.68	-0.26	100.06
	333			105.26
	353			110.46
Sugar	313	3.85	-0.31	100.88
	333			107.08
	353			113.28
Tea and Sugar	313	29.04	-0.23	101.03
	333			105.63
	353			110.23

*) Calculate using equation (6)

Fig. 1 shows the activation enthalpy against the activation entropy for vitamin C degradation in wedang jeruk. This relationship is represented by a linear equation y=315.55x+100.51. From this equation, it can be concluded that the slope is 315.55. According to equation (7) the slope of this equation is isokinetic temperature. In the other hand, using equation (8) we can determine the harmonic temperature and obtain that the harmonic temperature is 332.20 K. The harmonic temperature is higher than the isokinetic temperature. This reaction driven by entropy. This reaction is unfavourable at low temperatures, but becomes favourable at higher temperatures.

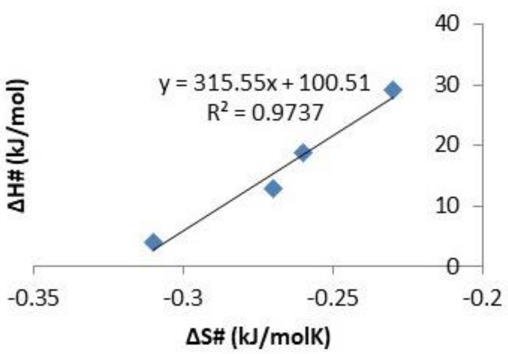

Figure 1. Enthalpy-entropy compensation for vitamin C degradation in wedang jeruk.

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4. Conclusion

The enthalpy of activation indicates that degradation of vitamin C includes endothermic processes. The value of enthalpy and entropy indicates the value of Gibbs-free energy is positive which means the reaction goes non-spontaneously. The harmonic temperature is higher than the isokinetic temperature. This reaction driven by entropy.

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