Research Article

Kinetics and Thermodynamics Study of Ultrasound-Assisted Depolymerization of κ-Carrageenan in Acidic Solution

R. Ratnawati[1,*], Nita Indriyani[2]

[1]Department of Chemical Engineering, Diponegoro University, Semarang, Indonesia.
[2]Department of Chemical Engineering, Faculty of Science and Technology, Universitas Pendidikan Muhammadiyah, Sorong, Indonesia.

Abstract

K-carrageenan is a natural polymer with high molecular weight ranging from 100 to 1000 kDa. The oligocarrageenan with low molecular weight is widely used in biomedical application. The aim of this work was to depolymerize κ-carrageenan in an acidic solution with the assistance of ultrasound irradiation. The ultrasonication was conducted at various pH (3 and 6), temperatures (30-60 °C), and depolymerization time (0-24 minutes). The results show that the depolymerization reaction follows pseudo-first-order kinetic model with reaction rate constant of 1.856×10^{-7} to 2.138×10^{-6} s^{-1}. The reaction rate constant increases at higher temperature and lower pH. The Q_{10}-temperature coefficients of the depolymerization are 1.25 and 1.51 for pH 6 and 3, respectively. The enthalpy of activation ($\Delta H^{\ddagger}$) and the Gibbs energy of activation ($\Delta G^{\ddagger}$) are positive, while the entropy of activation ($\Delta S^{\ddagger}$) is negative, indicating that the activation step of the ultrasound-assisted depolymerization of κ-carrageenan is endothermic, non-spontaneous, and the molecules at the transition state is more ordered than at the ground state. The $\Delta H^{\ddagger}$ and the $\Delta S^{\ddagger}$ are not affected by temperature, while the $\Delta G^{\ddagger}$ is a weak function of temperature. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ become smaller at higher pH, while the $\Delta G^{\ddagger}$ increases with the increase of pH. The kinetics and thermodynamics analysis show that the ultrasound-assisted depolymerization of κ-carrageenan in acidic solution is possibly through three mechanisms, *i.e.* bond cleavage due to cavitational effect of microbubbles, hydroxyl radical and hydrogen peroxide, as well as proton. Copyright © 2020 BCREC Group. All rights reserved

1. Introduction

K-carrageenan is a natural hydrocolloid with an average molecular weight of 100-1000 kDa extracted mainly from red seaweed (*Kappaphycus alvarezii*). It is basically a linear sulfated polysaccharide with disaccharide as the repeating unit, consisting of 3-linked α-D-galactose 4-sulfate (G4S) and 4-linked 3,6-anhydro-β-galactopyranose (AG). It is widely used in food, cosmetic, and pharmaceutical industries [1]. However, the utilization of κ-carrageenan in biomedical application is limited because of its high molecular weight.

* Corresponding Author.
  E-mail: ratnawati@che.undip.ac.id (R. Ratnawati);
  Telp: +62-24-7460058, Fax: +62-24-76480675

Many researchers have attempted to apply low molecular weight κ-carrageenan in biomedical field as tumor growth inhibitor [2], antivirus [3], anticoagulant, antioxidant [4], and cancer growth inhibitor [5]. The biological activity of carrageenans is influenced by the degree of sulfation, distribution of sulfate groups in the carbohydrate backbone, and the molecular weight [3]. It is hypothesized that the bioactivity of the low molecular weight κ-carrageenan against virus is due to the negative charge of the molecule which may effectively inhibit reverse transcriptase enzyme activity of the virus [1]. Furthermore, κ-carrageenans with lower molecular weights have better antioxidant activity and potential for cancer prevention [5].

K-carrageenan can be depolymerized using various techniques, such as thermal depolymerization [6], acid-catalyzed hydrolysis [7-11], enzymatic hydrolysis [2], ozone oxidation [12], and ultrasound irradiation [13]. When a polysaccharide solution is subjected to an ultrasound irradiation, the ultrasound wave will cause a cavitation which consists of the nucleation, growth, and collapse of microbubbles. This special acoustic cavitation effect is able to cleave the polymer chain at the midpoint [14]. The collapse of the bubbles also generates instantaneous hotspot with a temperature of 5000 K and pressure of 1000 atm inside the bubbles, while the temperature in the vicinity of the collapsing bubbles can reach 1000 K. This hotspot is able to induce dissociation of water molecules to hydrogen and hydroxyl radicals [15].

Ratnawati *et al.* [13] investigated the effect of temperature on the thermodynamics and kinetics of depolymerization of κ-carrageenan at pH 9 with the assistance of ultrasound irradiation. There has been no researcher concerned on the effect of pH on the ultrasound-assisted of hydrolysis of k-carrageenan. Therefore, this research is aimed to study the effect of pH along with the temperature on the kinetics and thermodynamics of ultrasound-assisted hydrolysis of κ-carrageenan.

2. Materials and Methods

2.1 Materials

Semi-refined κ-carrageenan used in this work was obtained from CV. Karagenan Indonesia, Semarang. Other materials used were hydrochloric acid solution 37% (E. Merck, Cat. No.100314), isopropyl alcohol (E. Merck, Cat. No.818766), and distilled water.

2.2 κ-carrageenan Refining

Prior to the depolymerization experiment, the κ-carrageenan was refined. Semirefined κ-carrageenan powder was dispersed in distilled water to form a 1% (w/v) mixture which was then heated at 80 °C for 15 minutes by constant stirring. The mixture was filtered using a vacuum filter to remove the undissolved matter. Isopropyl alcohol was added to the filtrate to coagulate the carrageenan which was then separated from the liquid by vacuum filtration. The carrageenan was dried in an air-forced dryer at 70 °C for 24 h and milled into 80 mesh and stored in a closed-tight container for the experiment.

2.3 Ultrasonication

The refined carrageenan powder was dispersed in distilled water to form a 0.5% (w/v) mixture. The mixture was heated and stirred at ±70 °C for ±15 minutes. The solution was adjusted to a certain temperature required for the ultrasonic experiment (30, 40, 50, and 60 °C). A dilute HCl solution was added to the κ-carrageenan solution to adjust the pH to 3 and 6. The solution was transferred to a glass vessel, which was then placed in an ultrasound device, Krisbow type KLS 303365 with a frequency of 42 kHz. The sonication was conducted for 24 minutes, and a sample was withdrawn in every 8 minutes for viscosity determination using a Canon-Fenske capillary viscometer. Each viscosity determination was conducted in triplicate.

2.4 Molecular Weight Determination

The viscosity of each sample was determined at various concentration, and the η_{sp}/c was plotted against c according to Huggins equation as written in Equation (1) [16]:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \qquad (1)$$

where c (g.mL^{-1}), η_{sp} (dimensionless), $[\eta]$ (mL.g^{-1}), and k_H (dimensionless) are the concentration, specific viscosity, intrinsic viscosity, and Huggins constant of the solution, respectively. The intrinsic viscosity was deduced from the intercept of the plot. The intrinsic viscosity is related to the number-average molecular weight (M) according to Mark-Houwink equation as presented in Equation (2).

$$[\eta] = KM^a \qquad (2)$$

where K and a are Mark-Houwink parameters. The values of K and a for κ-carrageenan in

aqueous solution at 25 °C are 0.00778 and 0.90, respectively [16].

2.5 Kinetics Model Development

The derivation of the kinetics model for ultrasound-assisted depolymerization of κ-carrageenan is based on the assumption that both glycosidic bonds, *i.e.* α(1→3) and β(1→4), have similar susceptibility to breakage by ultrasound and acid hydrolysis [17]. The model to describe the kinetics of the depolymerization of κ-carrageenan under the influence of ultrasound irradiation follows pseudo-first order kinetic is represented by Equation (3) [13],

$$\frac{1}{M_t} = \frac{1}{M_0} + \left(\frac{k}{m}\right)t \qquad (3)$$

where k is the rate constant, m is the molecular weight of the structural unit and M_0 and M_t are the number-average molecular weight of the polymer at $t = 0$ and t, respectively. The repeating unit in κ-carrageenan consists of G4S and AG units with molecular weights of 241 and 144, respectively. Since both the α(1→3) and β(1→4) links have similar susceptibility to breakage, an average of the molecular weights of both structural units is used here, *i.e.* 192 [6,17].

The rate constant (k) can be related to temperature according to Arrhenius equation as presented in Equation (4),

$$k = Ae^{-E_a/RT} \qquad (4)$$

where A is the pre-exponential factor (s⁻¹), E_a is the activation energy (kJ.mol⁻¹), and R is the universal gas constant ($8.314×10^{-3}$ kJ.mol⁻¹.K⁻¹).

2.6 Thermodynamics Parameters

The rate constant can be related to Gibbs energy of activation ($\Delta G^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and entropy of activation ($\Delta S^\ddagger$) by the Eyring transition state theory as presented by Equation (5) [18]:

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \qquad (5)$$

where k_B and h are Boltzmann constant ($1.3806×10^{-23}$ J.K⁻¹) and Planck constant ($6.626×10^{-34}$ J.s), respectively.

3. Results and Discussions

3.1 Kinetics of κ-carrageenan Depolymerization

Equation (3) is used to correlate the number-average molecular weight of κ-carrageenan and time of ultrasonication. The rate constant (k) can be obtained by plotting of $1/M_t$ versus t as depicted in Figure 1. The values of k for various pH and temperatures of this work are presented in Table 1. The Arrhenius plot of ln (k) versus $1/T$ is depicted in Figure 2. The pre-exponential factor A and the activation energy E_a are obtained from the intercept and slope of the plot, respectively, and are presented in Table 2 along with the results for pH 9 calculated using the data from the literature [13].

3.1.1 Effect of temperature on the rate constant
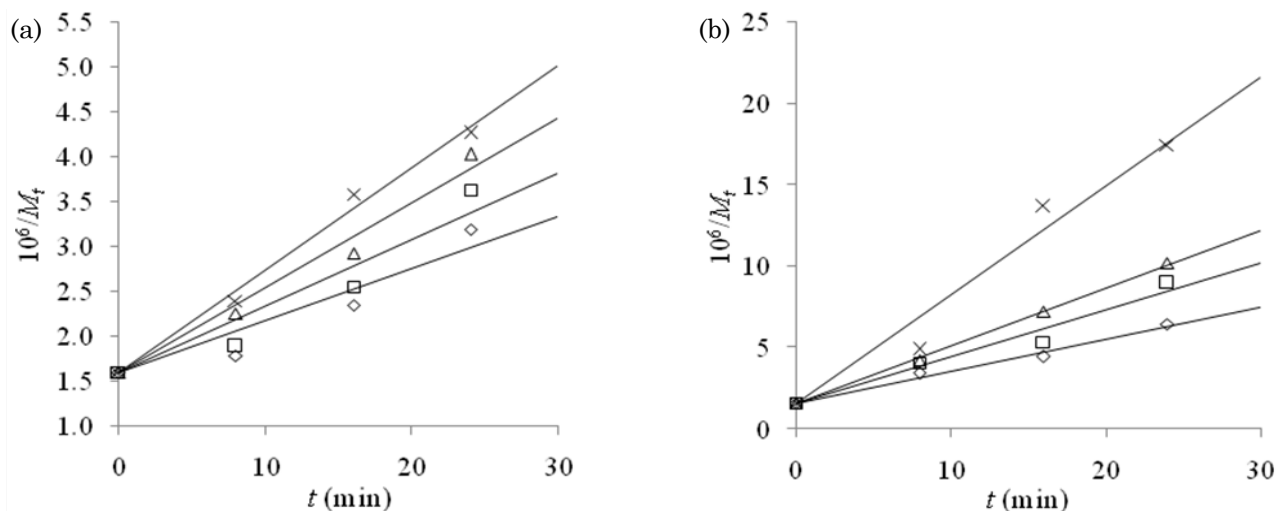
The results presented in Table 1 show that

Figure 1. Kinetics of ultrasound-assisted acid hydrolysis of κ-carrageenan at (a) pH 6 and (b) pH 3 (◊ 30°C; □ 40°C; Δ 50°C; × 60°C)

the rate constant (k) is influenced by temperature. To examine the effect of temperature on the reaction rate constant, the Q_{10}-temperature coefficient is commonly used [19], which is defined in Equation (6),

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{T_2 - T_1}} \qquad (6)$$

where k_1 and k_2 are the reaction rate constants at temperatures T_1 and T_2, respectively. The rate constant for pH 3 increases from 6.24×10^{-7} s^{-1} at 30 °C to 2.138×10^{-6} s^{-1} at 60 °C, or the Q_{10}-temperature coefficient is 1.51. Meanwhile, the rate constant for pH 6 rises from 1.856×10^{-7} s^{-1} at 30 °C to 3.648×10^{-6} s^{-1} at 60 °C, or the Q_{10}-temperature coefficient is 1.25. The Q_{10}-temperature coefficients obtained in this work along with those calculated from the literature for the ultrasound-assisted depolymerization [13] and those for thermal and acid hydrolysis without the assistance of ultrasound [6,8,9] are presented in Table 3.

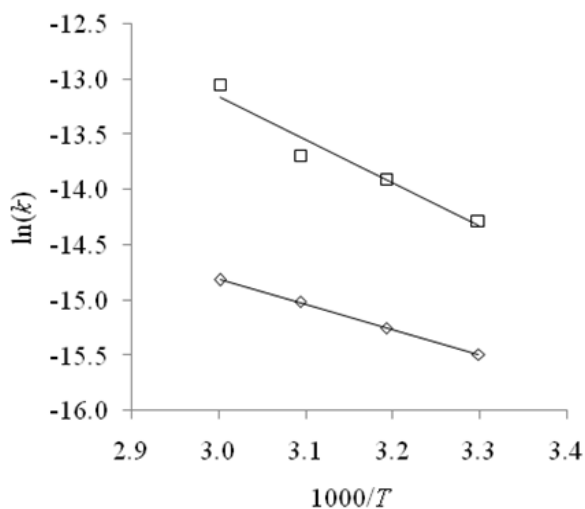Many groups of researchers revealed similar results to this work, in which the rate constant increased as the temperature became higher [13,18,20,21]. Ratnawati *et al.* [13] depolymerized κ-carrageenan at 30-60 °C and pH 9 and found that the Q_{10}-temperature coefficient was 1.16. The mechanism possibly occurred causing the reaction became faster when the temperature increased was through the radical formation [13]. During cavitation of microbubbles, accompanied with instantaneous extremely high temperature (up to 5000 °C) and pressure (up to 1000 atm) [15], the water molecule may experience homolytic bond breaking to hydrogen radical (H•) and hydroxide radical (OH•) leading to the formation of hydrogen gas (H$_2$) and hydrogen peroxide (H$_2$O$_2$) [22]. The hydroxyl radical and hydrogen peroxide are strong oxidizing agents [23]. Both oxidants are able to depolymerize organic polymer by cleaving the glycosidic bond [24,25]. This oxidation reaction is accelerated as the temperature rises [25].

Wang *et al.* [18], Waghmare and Rathod [20], and Prajapat *et al.* [21] conducted sonoenzymolysis to starch at 25-65 °C, waste cooking oil at 40-60 °C, and guar gum at 30-50 °C, respectively. The Q_{10}-temperature coefficient value of 1.47 can be calculated from the data of Wang *et al.* [18], 1.16 from Waghmare and Rathod [20], and 1.14 from Prajapat *et al.* [21]. They explained that a higher temperature could reduce the viscosity of the reaction mixture that would enhance the interactions between the enzyme and the substrate. This would make the reaction proceed faster and hence higher value of the rate constant at higher temperature was observed [20,21].

However, there are different results reported by other researchers. Mahalik and Madras [26] degraded poly(butyl acrylate) in o-dichlorobenzene and found that the rate constant decreased from 2.95×10^{-7} mol.g^{-1}.min^{-1} to 1.38×10^{-7} mol.g^{-1}.min^{-1} as the temperature increased from 30 to 70 °C, or the Q_{10}-temperature coefficient was 0.83. Chakraborty *et al.* [27] found that the Q_{10}-temperature coefficient for degradation of isotactic polypropylene and polybutadiene were also less than uni-

Figure 2. Arrhenius plot of ultrasound-assisted acid hydrolysis of κ-carrageenan (□ pH 3; ◊ pH 6).

Table 1. Rate constants of reactions at various pH and temperatures.

T (°C)	pH 3		pH 6	
	k (s^{-1})	R^2	k (s^{-1})	R^2
30	6.240×10^{-7}	0.985	1.856×10^{-7}	0.903
40	9.120×10^{-7}	0.965	2.638×10^{-7}	0.913
50	1.126×10^{-6}	0.998	3.008×10^{-7}	0.978
60	2.138×10^{-6}	0.961	3.648×10^{-7}	0.989
Overall		0.977		0.946

Table 2. Activation energy and pre-exponential factor of ultrasound-assisted depolymerization of κ-carrageenan at various pH.

Parameter	This work		[13]
	pH 3	pH 6	pH 9
E_a (kJ.mol^{-1})	32.63	19.04	12.39
A (s^{-1})	2.506×10^{-1}	3.566×10^{-4}	3.997×10^{-6}

ty, *i.e.* 0.85 and 0.77, respectively. These groups of researchers explained that the reduction of depolymerization rate as the temperature rise was possibly due to the nature of the mechanism causing the polymer chain scission at the midpoint. As the temperature increases, more solvent evaporates and enters the cavitation bubbles. This will cause a cushioning effect on the collapsing bubbles and a diminishing of the intensity of the shock wave. It eventually lessens the degradation rate of the polymer at higher temperatures. Furthermore, these researchers used organic solvents instead of water. It is possible that the organic solvent does not experience cleavage as water, so there are no oxidizing agents, such as: hydroxyl radical and hydrogen peroxide formed during the ultrasonication. As the results, the only reaction that might happen was due to the mechanical effect of collapsing microbubbles, which is negatively affected by temperature.

It is presented in Table 3 that the Q_{10}-temperature coefficients for chemical depolymerization of κ-carrageenan in aqueous solution with the assistance of ultrasound range from 1.16 to 1.51 while those without ultrasound vary from 3.19 to 3.54. Meanwhile, the Q_{10}-temperature coefficients of the ultrasound-assisted depolymerisation of various polymers in organic solvents are less than unity. It indicates that the chain scission mechanism happening in organic solvent, *i.e.* midpoint scission due to solvatodynamic effect of the collapsing microbubbles, also occurs in the ultrasound-assisted depolymerisation of κ-carrageenan in aqueous solution [13].

3.1.2 Effect of pH on the rate constant

The results presented in Table 3 indicate that pH also affects the rate constant. At the same temperature, the rate constant increases as the pH decreases. At 30 °C the rate constant increases from 1.856×10^{-7} s^{-1} at pH 6 to 6.240×10^{-7} s^{-1} at pH 3. The same effects are observed for other temperatures. At pH lower than 7, another mechanism, *i.e.* acid hydrolysis, may also occur. According to Yoon *et al.* [28], the proton (H$^+$) readily attacks oxygen in the glycosidic bond causing cleavage at the bond. The concentration of proton at pH 3 is higher than that at pH 6, hence the reaction is faster at pH 3 than at pH 6.

It is presented in Table 1 that pH affects the Q_{10}-temperature coefficients. At the same range of temperature (30-60 °C), the Q_{10}-temperature coefficients increases from 1.25 at pH 6 to 1.51 at pH 3. Meanwhile, a value of 1.16 for the Q_{10}-temperature coefficients at pH 9 (at 30-60 °C) can be calculated based the work of Ratnawati *et al.* [13]. It indicates that the Q_{10}-temperature coefficient increases as the pH decreases. A similar effect in acid hydrolysis of κ-carrageenan without ultrasound can also be deduced based on the data in the literature [8,9] as presented in Table 3. At almost the same range of temperature (54-78 °C), the Q_{10}-temperature coefficients are 3.19 at pH 4.7 [9], 3.36 at pH 3 [9], and 3.54 at pH 2 [8]. The increase of the Q_{10}-temperature coefficient at lower pH is most possibly due to the difference in proton concentrations. The concentration of proton at pH 2 is 2.7-order of magnitude higher than that at pH 4.7. With a higher concentration of proton, more glycosidic oxygens are attacked by the proton. This reaction proceeds faster as the temperature becomes higher [29]. As a result, the Q_{10}-temperature coefficient becomes higher at lower pH. The Q_{10} lowering effect of pH on the ultrasound-assisted depolymerization of κ-carrageenan is most possibly through the mechanism happens in the depolymerization without the assistance of ultrasound. As pH lowers, the concentration of proton increases causing more cleavage of carrageenan molecules as a result of proton attack to oxygen at the glycosidic bond. This reaction, as other chemical reactions, proceeds faster as the temperature becomes higher. As a result, the Q_{10}-

Table 3. The Q_{10}-temperature coefficient for the hydrolysis of κ-carrageenan.

| T (°C) | pH | Q_{10}-temperature coefficient | | Ref. |
		With ultrasound	Without ultrasound	
30-60	3	1.51		This work
30-60	6	1.25		This work
30-60	9	1.16		[13]
55-75	2		3.54	[8]
59-78	3		3.36	[9]
54-75	4.7		3.19	[9]

temperature coefficient increases as the pH decreases.

3.1.3 Effect of ultrasound on the rate constant

The Q_{10}-temperature coefficients for hydrolysis with the assistance of ultrasound at pH 3 and 9 are 1.51 and 1.16, respectively as presented in Table 3. Meanwhile, for hydrolysis without ultrasound, the values are 3.54 at pH 2 [8] and 3.19 at pH 4.7 [9]. In general, the Q_{10}-temperature coefficients for the ultrasound-assisted depolymerisation are lower than that of the depolymerisation without the assistance of ultrasound. It indicates that ultrasound lowers the Q_{10}-temperature coefficients. Choi and Kim [30], who hydrolyzed starch in 3% H_2SO_4 solution, also found a similar effect in which ultrasound lowered the Q_{10}-temperature coefficient from 3.10 for hydrolysis without ultrasound to 2.40 for hydrolysis with ultrasound. The occurrence of the polymer bond cleavage due to physical effect of the shear stress of the collapsing bubble in the ultrasound-assisted hydrolysis is possibly the cause of the lower value of the Q_{10}-temperature coefficient compared to that of the hydrolysis without the assistance of ultrasound. It means that the cleavage of κ-carrageenan through cavitational effect of the microbubble possibly occurs in the ultrasound-assisted acid hydrolysis of κ-carrageenan [13].

3.2 Thermodynamics of κ-carrageenan Depolymerization

3.2.1 Effect of ultrasound on activation energy

The results presented in Table 2 show that the value of E_a for ultrasound-assisted hydrolysis of κ-carrageenan at pH 3 and 6 are 32.63 kJ.mol^{-1} and 19.04 kJ.mol^{-1}, respectively. The value of 12.39 kJ.mol^{-1} was calculated for the pseudo-first-order kinetic model using the data of hydrolysis of κ-carrageenan at pH 9 [13]. Most of the chemical reactions, without the assistance of ultrasound, have activation energy which varies from 40 to 400 kJ.mol^{-1}. A reaction is categorized as a very fast reaction when its E_a is less than 40 kJ.mol^{-1} [21].

To evaluate the effect of ultrasound on the thermodynamics parameters of hydrolysis of κ-carrageenan, this work is compared to that reported by Lai *et al.* [6] who performed thermal hydrolysis of κ-carrageenan at pH 7 without ultrasound. They found that E_a and A were 97 kJ.mol^{-1} and 7.0×10^7 s^{-1}, respectively. Comparing the result of this work at pH 6, with E_a equals 19.04 kJ.mol^{-1} and A as low as

3.566×10^{-4} s^{-1}, to those obtained by Lai *et al.* [6], it is obvious that ultrasound lowers both the activation energy and the pre-exponential factor. A similar effect was reported by Wang *et al.* [18] who conducted an enzymolysis to starch with and without ultrasound. They reported that E_a for the enzymolysis at 25-55 °C without and with ultrasound were 46.71 kJ.mol^{-1} and 40.92 kJ.mol^{-1}, respectively. The reduction of the activation of energy in the ultrasound-assisted hydrolysis means that ultrasound may reduce the energy barrier for reaction. According to transition state theory, a chemical reaction proceeds through the formation of a transition complex. This step needs an amount of energy, known as the activation energy. The scission of the polymer molecules by cavitation effect of ultrasound does not go through the formation of the activated complex, so it does not have any energy barrier [21].

The activation energy of the ultrasound-assisted depolymerization of κ-carrageenan obtained in this work and that obtained from the literature [13] are higher than those of the ultrasound-assisted depolymerization of polymers in organic solvents, but less than those of most of the chemical reactions without the assistance of ultrasound. The activation energy for ultrasound-assisted depolymerization of polypropylene, polybutadiene, poly(n-butyl acrylate), and poly(butyl methacrylate) were all negative [26,27,31]. The negative value of the activation energy would not have any physical meaning, but it is similar to that observed for mechanical breakage of polymer [27]. It also indicates that the mechanism through cavitation effect, which is a physical process, dominates the ultrasound-assisted depolymerization in organic solvents. The activation energy obtained in this work is 19.04-32.63 kJ mol^{-1}. It is obvious that mechanism other than the physical effect of cavitation could possibly occur as well, *i.e.* oxidation by hydroxyl radical and hydrogen peroxide as explained previously, as well as the attack of the glycosidic oxygen by the proton.

3.2.2 Effect of pH on activation energy

At pH 9, the activation energy of ultrasound-assisted depolymerization of κ-carrageenan calculated from the data reported by Ratnawati *el al.* [13] is 12.39 kJ.mol^{-1}. The positive value of the activation energy could be due to the contribution of the chemical reaction. At pH 9, the concentration of proton is extremely low, *i.e.* 10^{-9} mol.L^{-1}, that the

mechanism through protonation of O in glycosidic bond is very likely not the case. The chemical reaction that most possibly occurs is the attack of κ-carrageenan molecules by hydroxyl radical and hydrogen peroxide as the results of homolytic cleavage of water molecules.

As it is shown in Table 2, the activation energy becomes higher at lower pH. It is possible that another mechanism with higher activation energy also works in this depolymerization. *i.e.* through the protonation of oxygen in glycosidic bond. As pH becomes lower, the number of proton increases causing more proton-catalyzed depolymerization, with high activation energy, to occur. The effect of all mechanisms is that the activation energy rises as the pH decreases. However, the pre-exponential factor is much lower for higher pH. Hence, the overall effect of pH on the rate constant is that the rate constant increases as pH decreases. Similar results were reported by L'homme *et al.* [32] for the hydrolysis of fructooligosaccharides in mineral-buffered aqueous solutions. The activation energy for the hydrolysis of 1-kestose increases from 75.4 to 80.9 kJ.mol^{-1} as the pH decreases from 7.0 to 4.0, while those for nystose and fructofuranosylnystose increase from 60.9 and 56.7 kJ.mol^{-1} to 76.2 and 84.6 kJ.mol^{-1}, respectively.

3.2.3 Effect of pH on $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$

The values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from the data of this work along with those from the literature [6,10,13] are presented in Table 4. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not affected by temperature, while $\Delta G^{\ddagger}$ is a weak function of temperature as presented in Table 4.

The enthalpy of activation ($\Delta H^{\ddagger}$) of the ultrasound-assisted acid hydrolysis of κ-carrageenan obtained in this work is positive. It means that the formation of the activated complex is an endothermic reaction. As presented in Table 4, the $\Delta H^{\ddagger}$ of the ultrasound-assisted depolymerization at pH 6 is 48% lower than that at pH 3. Meanwhile, from the pseudo-first-order kinetic model of the ultrasound-assisted depolymerization at pH 9 as reported by Ratnawati *et al.* [13], the $\Delta H^{\ddagger}$ can be calculated, *i.e.* 9.74 kJ.mol^{-1}. These results show that pH affects the $\Delta H^{\ddagger}$. The $\Delta H^{\ddagger}$ becomes lower as the pH becomes higher. At pH 9, the possible reaction mechanisms are through physical scission by shear stress in the vicinity of the collapsing microbubbles [15] and oxidative scission by hydroxyl radical and hydrogen peroxide [22]. The physical reaction does not need activation energy, but the oxidative reaction is most likely the mechanism that needs the activation energy, and as the result is that the $\Delta H^{\ddagger}$ of the depolymerization at pH 9 is as low as 9.74 kJ.mol^{-1}. As the pH lowers, more protons exist in the solution, which promote another mechanism, *i.e.* acid-catalyzed hydrolysis of κ-carrageenan with a higher value of activation energy, as well as the enthalpy of activation. As the result, the overall effect is that the $\Delta H^{\ddagger}$ is higher as pH becomes lower. The high value of $\Delta H^{\ddagger}$ of acid-catalyzed hydrolysis of κ-carrageenan was confirmed by the result of

Table 4. Thermodynamic parameters for hydrolysis of κ-carrageenan.

	pH	T (°C)	$\Delta H^{\ddagger}$ (kJ.mol^{-1})	$\Delta S^{\ddagger}$ (kJ.mol^{-1}.K^{-1})	$\Delta G^{\ddagger}$ (kJ.mol^{-1})	Ref.
With ultrasound	3	30 40 50 60	29.99	-0.265	110.40 113.05 115.71 118.36	This work
	6	30 40 50 60	15.56	-0.322	113.22 116.45 119.66 122.89	This work
	9	30 40 50 60	9.74	-0.357	118.00 121.57 128.14 128.71	[13]
Without ultrasound	2	35 55	102.3	-0.044	116.00 116.90	[10]
	7	75 85 95	96.4	-0.098	130.70 131.70 132.70	[6]

Hjerde *et al.* [8] (120 kJ.mol^{-1}) and Lai *et al.* [6] (97 kJ.mol^{-1}) who conducted thermal hydrolysis of κ-carrageenan at pH 2 and 7, respectively.

The value of $\Delta S^{\ddagger}$ is smaller (larger negative) as pH becomes higher as presented in Table 4. The negative value of $\Delta S^{\ddagger}$ indicates that the molecules at the transition state is more ordered than at the ground state [33]. At pH 9, as explained previously, the depolymerization is possibly through cavitation and radical reaction mechanisms. The bond cleavage by cavitation effect can only occur when the κ-carrageenan molecules is in a precise position relative to the shear stress induced by the collapsing bubbles, *i.e.* the midpoint of the polymer is close enough to the collapsing bubbles [14]. As pH becomes lower, the proton-catalyzed mechanism is more pronounced. It is most likely that the transition state of species involved in this mechanism is less ordered than that in the mechanical scission mechanism by microbubbles collapse. As the result, the overall activation entropy change is higher at lower pH.

To evaluate the effect of ultrasound on the activation entropy, the $\Delta S^{\ddagger}$ at pH 6 of this work is compared to that calculated from the data reported by Lai *et al.* [6]. The activation entropy calculated from the data of Lai *et al.* [6] (-0.10 kJ.mol^{-1}.K^{-1}) is much larger than the value obtained in this work (-0.322 kJ.mol^{-1}.K^{-1}). It indicates that ultrasound lowers the activation entropy, which means that more molecules are in ordered configuration during the depolymerization reaction, *i.e.* through the mechanical scission mechanism by microbubbles collapse.

The values of $\Delta G^{\ddagger}$ of the ultrasound-assisted depolymerization, as presented in Table 4, are all positive. It means that the ultrasound-assisted depolymerization of κ-carrageenan is a non-spontaneous and endergonic process [33]. At the same temperature, $\Delta G^{\ddagger}$ decreases with pH. On average, the values of $\Delta G^{\ddagger}$ at pH 3 is 3.1% lower than those of pH 6. The same effect is also observed in the depolymerization of κ-carrageenan without the assistance of ultrasound [6,9] as presented in Table 4.

4. Conclusions

The ultrasound-assisted of acid hydrolysis of k-carrageenan has been conducted. The depolymerization reaction follows a pseudo-first order reaction. It is found that the higher temperature increases the reaction rate constant. The effect of temperature on the reaction rate constant can be measured by the Q_{10}-temperature coefficient of which the value is greater than unity. It is also concluded that as the pH lowers, the reaction rate constant becomes higher as well as the Q_{10}-temperature coefficient. Based on kinetics and thermodynamics analysis, the depolymerization of κ-carrageenan in acidic solution with the assistance of ultrasound is most possibly through three mechanisms, *i.e.* bond cleavage due to cavitational effect of microbubbles, hydroxyl radical and hydrogen peroxide, as well as proton. The reaction rate constant has a positive correlation to temperature. Lower pH gives a higher value of the Q_{10}-temperature coefficient. At higher pH, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ become smaller while $\Delta G^{\ddagger}$ becomes slightly higher. The $\Delta H^{\ddagger}$ is positive, indicating that the activation reaction is endothermic. The $\Delta G^{\ddagger}$ is a weak function of temperature and positive, indicating that the activation reaction is non-spontaneous and endergonic.

Acknowledgments

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