Kinetics and Thermodynamics of Ultrasound-Assisted Depolymerization of κ-Carrageenan

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Abstract

The ultrasound-assisted depolymerization of κ-carrageenan has been studied at various temperatures and times. The κ-carrageenan with initial molecular weight of 545 kDa was dispersed in water to form a 5 g/L solution, which was then depolymerized in an ultrasound device at various temperatures and times. The viscosity of the solution was measured using Brookfield viscometer, which was then used to find the number-average molecular weight by Mark-Houwink equation. To obtain the kinetics of κ-carrageenan depolymerization, the number-average molecular weight data was treated using midpoint-chain scission kinetics model. The pre-exponential factor and activation energies for the reaction are $2.683 \times 10^{-7} \text{ mol g}^{-1} \text{ min}^{-1}$ and 6.43 kJ mol$^{-1}$, respectively. The limiting molecular weight varies from 160 kDa to 240 kDa, and it is linearly correlated to temperature. The results are compared to the result of thermal depolymerization by calculating the half life. It is revealed that ultrasound assisted depolymerization of κ-carrageenan is faster than thermal depolymerization at temperatures below 72.2°C. Compared to thermal depolymerization, the ultrasound-assisted process has lower values of $E_a$, $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$, which can be attributed to the ultrasonically induced breakage of non-covalent bonds in κ-carrageenan molecules. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: Depolymerization; Half life; Limiting molecular weight; Midpoint-chain scission; κ-carrageenan

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1. Introduction

Carrageenan is a sulfated galactan extracted from red algae (Rhodophyceae), which is abundantly available in Indonesian waters. The basic structure of carrageenan is potassium, sodium, calcium, magnesium, or ammonium sulfate ester of D-galactose polymer linked in α-1,3 and β-1,4 positions. The structure is depicted in Figure 1.

Carrageenan is utilized in food industries as thickening, gelling, and stabilizing agents [1]. Attempts have been conducted to broaden the utilization of carrageenan, one of which is through depolymerization. The oligomers or the low molecular weight fraction (LMWF) of carrageenan as the result of depolymerization is subjected to biomedical applications. It was reported that the LMWF carrageenan had activity to inhibit tumor growth [2-4]. The LMWF carrageenan was also reported to have antiher-

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Cavitation 

Cavitation is the rapid collapse of bubbles that occur when ultrasound is irradiated to a liquid. This phenomenon is characterized by the formation of bubbles in the liquid phase, which then collapse, releasing energy in the form of a shock wave. The hot spot generated by the collapse of cavitation bubbles is capable of breaking covalent bonds in polymers, allowing for depolymerization. This process is known as ultrasound-assisted depolymerization. The collapse of cavitation bubbles is dependent on the temperature and pressure, which can reach as high as 5000 K and 1000 atm, respectively. The collapse of cavitation bubbles is accompanied by intense local heating and high pressures, which can cause dissociation of water molecules to give hydroxyl radicals.

The reports on the study of the effect of temperature on the kinetics and thermodynamics of ultrasound-assisted depolymerization of κ-carrageenan are not available in the literature to the moment. Therefore, the aim of this work is to study the effect of temperature on the kinetics and thermodynamics of ultrasound-assisted depolymerization of κ-carrageenan.

2. Materials and Methods

2.1. Materials

The raw material used in this work was κ-carrageenan derived from seaweed Kappaphycus alvarezii, which was produced by CV. Karagen Indonesia, Semarang, Indonesia. The carrageenan was dissolved in distilled water to form a 5 g/L solution. The solution was placed in a 40 mm diameter and 120 mm height glass vessel. The mixture was heated to 60°C and stirred for 15 minutes.

2.2. Ultrasound treatment

Two hundred milliliters of sample was brought to specified temperatures (30, 40, 50, 60°C).
2.3. Measurement of viscosity

The viscosity of the k-carrageenan in aqueous 0.1 M NaCl solution was measured using Brookfield viscometer of RDVE model. The solution was put in the sample container placed in water bath to equilibrate the temperature to 65 ± 0.1°C. Spindle number 2 was then immersed into the sample to the groove of the shaft. The speed of the spindle was set at 60 rpm, then the viscometer was started and the reading was made at constant reading. The measurement was done in triplicate.

2.4. Mathematical treatment for intrinsic viscosity

The intrinsic viscosity \([\eta]\) was calculated from the specific viscosity \((\eta_s)\) obtained from the Brookfield viscometer readings. The intrinsic viscosity is the average intercept of Huggins and Kraemer equation [35] in Equation (1).

\[
\frac{\eta_s}{c} = [\eta] + k_H [\eta]^2 c
\]  

(1)

where \(\eta_s\), \([\eta]\), \(k_H\), and \(c\) are specific and intrinsic viscosity, Huggins constant, and the concentration of the solution, respectively. The specific viscosity \((\eta_s)\) and the Huggins constant \((k_H)\) are dimensionless, while the intrinsic viscosity \(([\eta])\) and the concentration \((c)\) have the units of mL/g and g/mL, respectively. The value of \(k_H\) for k-carrageenan solution is 0.35 [35].

The molecular weight of k-carrageenan \((M)\) is related to its viscosity by Mark Houwink equation [35] in Equation (2).

\[
[\eta] = k_{MH} M^\alpha
\]  

(2)

where \(k_{MH}\) and \(\alpha\) are constants for a given system. In this work, the values of \(k_{MH}\) and \(\alpha\) for k-carrageenan are 0.00598 and 0.90, respectively. \(M\) and \([\eta]\) are expressed in g/gmol and mL/g, respectively [20].

2.5. Mathematical treatment for kinetics model

In a depolymerization, all bonds of a polymer chain are equally susceptible to break with the rate proportional to the remaining unbroken bonds following a pseudo-first-order rate relation [36] in Equation (3).

\[
\frac{d(N_0, p)}{dt} = k_{pf} N_0, p
\]  

(3)

where \(N_0\) denotes initial number of monomer in the reaction mixture, \(p\) is fraction of monomers bonded in polymers, and \(k_{pf}\) is the pseudo-first-order reaction rate constant. The equation can be integrated from \(t = 0\) to \(t = t\) to yield Equation (4).

\[
P = P_0 e^{-k_{pf}t}
\]  

(4)

For short reaction time with only small fraction of bonds is broken, \(e^{-k_{pf}t}\) can be approximated by \(1 - k_{pf}t\), and Equation (4) becomes Equation (5).

\[
P = P_0 (1 - k_{pf}t)
\]  

(5)

Fraction of monomers bonded in polymers, \(p\), can be related to number-average molecular weight of polymer [36] as Equation (6).

\[
p = 1 - \frac{m}{M_t}
\]  

(6)

where \(M_t\) is the number-average molecular weight of polymer at time \(t\) and \(m\) is the average molecular weight of monosaccharide unit. Based on the assumption that \(a (1 \rightarrow 3)\) and \(\beta (1 \rightarrow 4)\) glycosidic linkages show similar susceptibility to breakage by ultrasound, the value of \(m\) is 192 [11, 20]. In terms of molecular weight of polymer, Equation (6) is simplified to Equation (7).

\[
\frac{1}{M_t} = \frac{1}{M_0} + \frac{k_{mf}}{m} t
\]  

(7)

where \(M_0\) is the number-average molecular weight of polymer at time 0. A plot of \(1/M_t\) versus \(t\) produces a linear relationship from which the rate constant can be deduced from the gradient.
Other model was developed based on mid-point-chain scission mechanism in mechanical degradation, for example, by ultrasonic radiation [37]. The degradation yields two molecules with nearly the same size. The breaking of the covalent bond of polymers continues up to a certain limiting molecular weight [22, 29], i.e. $M_c$. Using a continuous distribution model, Chakraborty et al. [29] derived the kinetics model in Equation (8).

$$\ln\left(\frac{1}{M_t} -\frac{1}{M_\infty}\right) = -k_m M_\infty t + \ln\left(\frac{1}{M_\infty} - \frac{1}{M_0}\right)$$ (8)

where $k_m$ is the reaction rate constant for mid-point-chain scission reaction model. A linear line is obtained by plotting $\ln\left(1/M_t - 1/M_\infty\right)$ versus $t$ where the rate constant can be obtained from the slope.

3. Results and Discussion

3.1. Effect of temperature on depolymerization

The variations of the number-average molecular weight of $\kappa$-carrageenan with sonication time at various temperatures are depicted in Figure 2. The molecular weight drops rapidly within the first 20 minutes but decreases slowly and at the end of the treatment the molecular weight approaches different limiting values for different temperatures. The results, as depicted in Figure 2, show that at higher temperatures, the molecular weight is lower than that at lower temperatures. It means that the extent of depolymerization at higher temperatures is higher as compared to lower temperatures.

The results are contradicted with those obtained by several groups of researcher who found that the extent of reaction decreased with increasing temperatures [29, 37-39]. They explained that the negative effect of temperature could be attributed to cavitation. As the temperature of the solution increases, more solvent vapor enters the cavitation bubble during the expansion and exerts a cushioning effect during the collapse leading to diminishing the intensity of the shock wave. It will reduce the jet velocity, which will further lessen degradation at higher temperatures [31, 37].

However, some other groups of researchers reported similar results to this work where temperature gives positive effect on ultrasound-assisted depolymerization [40-44]. In general, ultrasound-assisted degradation of organic polymers takes place via two mechanism, i.e., homolytic bond breaking and reaction with radicals [45-47]. The homolytic bond breaking reaction is usually caused by the cavitation of micro-bubbles accompanied with extremely high temperature (up to 5000 °C) and pressure (about 5x10^7 Pa) [12], which will lead to the second mechanism, i.e. the generation of H· and OH· radicals through thermal dissociation of water at the bubble/water interface. The main reactions during sonication are described in Equations (9-11) [45].

$$\text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^\bullet$$ (9)
$$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$$ (10)
$$\text{OH}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2$$ (11)

Both OH· radical and hydrogen peroxide are strong oxidizing agents. Even in a very low concentration, both OH· and H2O2 can oxidize organic polymer such as $\kappa$-carrageenan [47] causing random degradation [37]. This oxidation reaction, as other chemical reactions, is remarkably accelerated as the temperature rises [48]. The temperature effect can also be related to the viscosity of the reaction mixture. At lower temperature the viscosity of aqueous solution is higher than that of higher temperature. A certain amount of energy is consumed in the process of disaggregation [41]. Therefore, increasing the mixture temperature during sonication will lead to more $\kappa$-carrageenan molecules degraded as observed in Figure 2.
3.2. Effect of temperature on reaction kinetics

Two kinetics models (Equations (7) and (8)) are employed in this work to describe the ultrasound-assisted depolymerization of κ-carrageenan. Plot of ln 1/M_t versus t and ln (1/M_∞ - 1/M_t) versus t at various temperatures depicted in Figure 3, clearly show excellent linearity. The depolymerization rate constants, the limiting molecular weights, and correlation factors for both models at various temperatures are listed in Table 1.

The results presented in Table 1 show that both models have comparable correlation coefficients, however, the correlation coefficient of the midpoint-chain scission model is slightly larger than that of pseudo-first-order model. The percent of average absolute deviation (%AAD) of both models are also calculated. It is defined as Equation (12).

\[
\%AAD = \left(\frac{Y_{exp} - Y_{calc}}{Y_{exp}}\right) \times 100\%
\]

where Y is the left-hand side of Equation (7) and Equation (8) for pseudo-first-order model and midpoint-chain scission model, respectively. Subscript exp and calc refer to experimental and calculated values, respectively. It is clear from Table 1 that the overall %AAD of midpoint-chain scission model is much smaller than that of pseudo-first-order model. It indicates that midpoint-chain scission model is more suitable for describing ultrasound-assisted depolymerization. It means that sonication leads to midpoint-chain scission of κ-carrageenan molecules.

![Figure 3](image-url)

**Figure 3.** Time dependencies of (a) 1/M_t according to pseudo-first-order model and (b) ln (1/M_∞ - 1/M_t) according to midpoint-chain scission model for κ-carrageenan at 30°C (◊), 40°C (□), 50°C (∆), and 60°C (○)

**Table 1.** Kinetics parameters for pseudo-first-order and midpoint-chain scission models

| Temperature (°C) | Pseudo-first-order model | Midpoint-chain scission model |
|------------------|--------------------------|-------------------------------|
|                  | k_pf (min⁻¹) | R²   | %AAD | k_ms (mol g⁻¹min⁻¹) | M_∞ (g/mol) | R²   | %AAD |
| 30               | 1.74×10⁻⁶  | 0.94 | 3.59 | 2.11×10⁻⁸  | 240,000     | 0.95 | 0.33 |
| 40               | 2.05×10⁻⁶  | 0.95 | 4.12 | 2.24×10⁻⁸  | 210,000     | 0.97 | 0.25 |
| 50               | 2.42×10⁻⁶  | 0.97 | 4.09 | 2.47×10⁻⁸  | 190,000     | 0.98 | 0.19 |
| 60               | 2.69×10⁻⁶  | 0.97 | 3.95 | 2.63×10⁻⁸  | 160,000     | 0.96 | 0.26 |
| Overall          | 0.96       | 3.94 |      | 0.97       | 0.26        |      |      |
As presented in Table 1, the limiting molecular weight \((M_\infty)\) decreases as temperature increases. It is shown in Figure 4 that the limiting molecular weight is a linear function of temperature, and it can be presented by Equation (13).

\[
M_\infty = -2600 T + 10^6
\]  

(13)

with a correlation coefficient of 0.99. As temperature increases, the oxidation reaction by hydroxyl radical which leads to random scission of \(\kappa\)-carrageenan increases as well. It means that at higher temperature more \(\kappa\)-carrageenan are degraded, hence the final molecular weight will be smaller.

The rate constant for midpoint-chain scission model, \(k_{ms}\), is slightly influenced by temperature. It rises from \(2.11 \times 10^{-8}\) to \(2.63 \times 10^{-8}\) mol g\(^{-1}\) min\(^{-1}\) as the temperature rises from 30 to 60 °C, or in average it only increases 1.1 fold for a temperature increment of 10 °C. The effect of temperature on the rate constant of ultrasound-assisted depolymerization is much lower than that of thermal depolymerization and acid hydrolysis. Singh and Jacobson [12] who degradated \(\kappa\)-carrageenan by acid hydrolysis in a LiCl/HCl pH 2 buffer solution found that the rate constant increased 3.8 fold for every 10°C of temperature increment, while Lai et al. [11] found 2.3 fold for thermal depolymerization of \(\kappa\)-carrageenan. The smaller effect of temperature on sonicated depolymerization compared to acid and thermal depolymerizations is mostly caused by the effect of cavitation as explained above.

The temperature dependence of the \(k_{ms}\) is given by the Arrhenius law as presented in Equations (14-15).

\[
k_{ms} = Ae^{-E_a/RT}
\]  

(14)

or

\[
\ln k_{ms} = \ln A - \frac{E_a}{RT}
\]  

(15)

where \(A\) and \(E_a\) are pre-exponential factor and activation energy, respectively. Plot of \(\ln k_{ms}\) versus \(1/T\) will result in a linear line, as depicted in Figure 5, with correlation coefficient of 0.99. The constants, \(A\) and \(E_a\), can be obtained from the intercept and slope, which are \(2.68 \times 10^{-7}\) mol g\(^{-1}\) min\(^{-1}\) and \(6.43\) kJ mol\(^{-1}\), respectively.

Most of the reactions have \(E_a\) value ranging from 40 to 400 kJ mol\(^{-1}\). If the value is less than 40 kJ mol\(^{-1}\), the reaction will complete very rapidly [44]. The activation energy obtained in this work is \(6.43\) kJ mol\(^{-1}\), while the activation energy for thermal degradation of \(\kappa\)-carrageenan obtained by Lai et al. is \(99.6\) kJ mol\(^{-1}\) [11]. The smaller value of activation energy for ultrasound-assisted depolymerization shows that ultrasound remarkably decreases the energy barrier required for the reaction [44]. The great reduction in \(E_a\) value by ultrasonic treatment indicates that the ultrasound-assisted reaction occur very easily. However, the work of Lai et al. [11] had revealed that the pre-exponential factor of the
Arrhenius correlation was $4.25\times10^0 \text{ min}^{-1}$ which is much higher than that of this work. It must have implication to the reaction rate.

To compare the performance of thermal and ultrasound-assisted depolymerization, the half life of $\kappa$-carrageenan undergoing both processes are calculated. Suppose that we have $\kappa$-carrageenan with initial molecular weight of 544,980 as used in this work that undergoes two different processes, i.e. thermal and ultrasound-assisted depolymerizations, at various temperatures. The half life ($t_{1/2}$) of $\kappa$-carrageenan undergoing thermal degradation is calculated using Equation (7) with $A$ and $E_a$ are $9.47\times10^0 \text{ min}^{-1}$ and 99.6 $\text{kJ mol}^{-1}$, respectively, while that for ultrasound-assisted degradation is calculated using Equation (8) with $A$ and $E_a$ are $2.68\times10^{-7} \text{ mol g}^{-1} \text{ min}^{-1}$ and 6.43 $\text{kJ mol}^{-1}$, respectively. The results are presented in Figure 6. At lower temperatures ($<72.2^\circ\text{C}$), the half life of $\kappa$-carrageenan undergoing ultrasound-assisted depolymerization is smaller than that of thermal depolymerization. It means that ultrasound-assisted depolymerization is faster than thermal depolymerization at lower temperatures.

3.3. Effect of temperature and ultrasound treatment on the thermodynamic parameters

According to transition state theory, the rate constant is related to the changes in enthalpy of activation ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) as presented by the Eyring equation [49].

$$k_m = \frac{k_B T}{h} e^{\Delta S^\ddagger/RT} e^{\Delta H^\ddagger/RT} \tag{16}$$

where $k_B$ is the Boltzmann constant (1.3806$\times10^{-23} \text{ J K}^{-1}$), and $h$ is the Planck constant (6.6207$\times10^{-34} \text{ J s}$). The Equation (16) can be written as in Equation (17).

$$\ln \frac{k_m}{T} = -\frac{\Delta H^\ddagger}{RT} + \ln \left( \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \right) \tag{17}$$

A plot of $\ln (k_m/T)$ versus $1/T$ will result in a linear line with correlation coefficient of 0.97 as depicted in Figure 7.

From the slope and the intercept of the line, enthalpy of activation ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) can be deduced. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for ultrasound-assisted depolymerization are 3.79 $\text{kJ mol}^{-1}$ and -413.5 $\text{J mol}^{-1} \text{ K}^{-1}$, respectively. For thermal degradation, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, as calculated from the results of Lai et al. [11], are 96.41 $\text{kJ mol}^{-1}$ and -132.6 $\text{J mol}^{-1} \text{ K}^{-1}$, respectively. The results for both reactions are presented in Table 2.

The enthalpy of activation ($\Delta H^\ddagger$) is the difference between the enthalpy of the transition state and the sum of the enthalpies of the reactants in the ground state. A large value of enthalpy of activation indicates that a large amount of energy to stretch, squeeze or even break the chemical bonds is needed for the formation of the transition state. The value of
\( \Delta H^\ddagger \) of the ultrasound-assisted depolymerization is 96.1% lower than that of thermal process. The decrease of \( \Delta H^\ddagger \) accompanying the sonication can be explained by a decrease of the energy barrier of the reaction. Sonication may induce cavitation effect which creates enormous shear forces that can break covalent bond [25, 43]. It means that sonication can make the reactants reach transition state with less energy, which is translated to the decrease of \( \Delta H^\ddagger \) [50].

The value of \( \Delta S^\ddagger \) of the ultrasound-assisted depolymerization is lowered by 211.8% compared to that of thermal process. Large and negative value of \( \Delta S^\ddagger \) indicates that the formation of the transition state requires the carrageenan molecules to adopt precise configurations relative to the shear force around the collapsing bubbles [51]. The decrease in \( \Delta S^\ddagger \) is also an indication of more orderly distributed \( \kappa \)-carrageenan molecules after ultrasound irradiation [50]. Smaller value of \( \Delta S^\ddagger \) confirms the smaller value of the pre-exponential factor of the Arrhenius equation, \( A \), for the ultrasonic depolymerization, as the pre-exponential factor is proportional to \( \exp(\Delta S^\ddagger /R) \) [52].

The values of \( \Delta G^\ddagger \) is calculated using the fundamental equation \([49]\) in Equation (18).

\[
\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger
\] (18)

The values of \( \Delta G^\ddagger \) of thermal and ultrasound-assisted depolymerizations, as presented in Table 2, slightly increase as the temperature increases. It is a consequence of the form of equation (18). The value of \( \Delta G^\ddagger \) of the ultrasound-assisted depolymerization is 2.4% in average lower than that of thermal process at 30°C. The difference becomes smaller as the temperature increases. The same trend was also found by Jin et al. [50]. These decreases in \( E_a, \Delta H^\ddagger, \Delta S^\ddagger \), and \( \Delta G^\ddagger \) can be attributed to the ultrasonically induced breakage of non-covalent bonds in \( \kappa \)-carrageenan molecules and to the oxidative reaction of \( \kappa \)-carrageenan by hydroxyl radical [42, 50].

4. Conclusions

The ultrasonic depolymerization of \( \kappa \)-carrageenan has been investigated. The molecular weight decreases rapidly within the first 20 minutes then slowly approaches different limiting molecular weight for different temperatures. The extent of depolymerization is higher at higher temperatures.

Correlated using the mid-scission model with average coefficient of correlation of 0.97, the rate constant only increases 1.1 fold for a temperature increment of 10°C. The activation energy, \( E_a \), and pre-exponential factor, \( A \), for the reaction are 6.43 kJ mol\(^{-1}\) and 2.68×10\(^{11}\) mol g\(^{-1}\) min\(^{-1}\), respectively. When compared to thermal degradation, the half life (\( t_{1/2} \)), of ultrasound-assisted depolymerization at lower temperatures (< 72.2 °C) is smaller. It means that ultrasound-assisted depolymerization is faster than thermal depolymerization at lower temperatures.

Thermodynamic review of the reaction shows that the \( \Delta H^\ddagger, \Delta S^\ddagger, \) and \( \Delta G^\ddagger \) of the ultrasound-assisted depolymerization are lower than those of thermal process. Compared to thermal process, the, and of the ultrasound-assisted depolymerization are lower by 96.1%, 211.8%, and 2.4%, respectively. These decreases are related to the ultrasonically induced breakage of non-covalent bonds in \( \kappa \)-carrageenan molecules.

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| Table 2. Thermodynamic parameters for ultrasound-assisted and thermal depolymerization |
|---------------------------------------------------------------|
| **Thermal depolymerization [11]** | **Ultrasound-assisted depolymerization (this work)** |
| \( \Delta H^\ddagger \) (kJ mol\(^{-1}\)) | 96.41 | 3.79 |
| \( \Delta S^\ddagger \) (J mol\(^{-1}\) K\(^{-1}\)) | -132.6 | -413.5 |
| \( \Delta G^\ddagger \) (kJ mol\(^{-1}\)) |  |
| at 30°C | 136.61 | 129.15 |
| at 40°C | 137.94 | 133.29 |
| at 50°C | 139.26 | 137.42 |
| at 60°C | 140.59 | 141.56 |

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