Depolymerization Kinetics of Aqueous Cassava Starch under Sonication Process using Free-Radical Depolymerization Model and its Correlation with Radical Production from Acoustic Cavitation

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Abstract. The technology of biopolymer degradation to produce its derivative compounds is an important topic nowadays. The use of environmentally friendly methods, such as sonication, is a promising method for obtaining biopolymer derivative compounds. Sonication creates acoustic cavitation in the liquid body to produce radicals and microjets that can substitute acid substances in the degradation process. Through the sonication process, starch-based compounds can be degraded to oligosaccharides and reducing sugars, which have a variety of benefits in the food, pharmaceutical, and fermentation industries. Many experiments have been conducted to investigate the role of sonication in starch degradation. However, there is much process model that can describe the role of sonication in depolymerization. This work aims to evaluate the ability of sonication in producing reducing sugars and lower-molecular-weight starch by using the Free-radical depolymerization model and correlating it with the production of radicals from acoustic cavitation. Experiments were carried out using horn-type sonication with a power of 500W with various amplitudes. The reducing sugar analysis was carried out by the DNS method and the average molecular weight was estimated with Ubbelohde viscosimetry. From the simulation results, sonication with 30% of the maximum amplitude gives the largest radical production, which well correlates with the production of reducing sugar. The experimental results show a maximum yield of reducing sugar of 0.570 g / L in the process using S30 for 60 minutes.

1. Introduction

The utilization of biomass derivative products has increased attention in the food and pharmaceutical industry [1]. Cassava starch is one of the most abundant polysaccharide resources derived by depolymerization or degradation into various valuable products such as soluble starch, modified starch, oligosaccharide, and reducing sugars [2]. The acid and enzyme method becomes the most common method to produce the starch derivative product [3]. Long processing time and chemical solvent waste become problems that can affect the efficiency of the process. Water-insoluble granule form of starch is often addressed as the main factor that caused these drawbacks. To overcome these problems, many methods have been proposed, including sonication [4], high shear mixing [5], and hydrothermal [6].

Sonication of starch has become an exciting topic as an attractive reaction medium and environmentally-friendly solvent for numerous applications. It utilizes an ultrasonic wave to give
acoustic pressure to create cavitation on the liquid body [7]. By high amount intensity energy transferred through this processed media, the cavitation produces a local hotspot to introduce microjets and radicals [8]. Microjets create high velocity of the liquid particle, so that erodes the material surface. Radicals can trigger various chemical reactions, including starch depolymerization. Several works have been focused on starch degradation using the sonication process, which successfully affects reducing sugar production, granule defect, microstructural properties change, and granule size reduction.

Although many sonication applications on starch degradation have been researched, it is essential to enhance the process controllability by developing the depolymerization kinetics model. This article concentrates on the depolymerization kinetics of cassava starch. We develop the free-radical induced depolymerization and the n-order depolymerization reaction. The model includes the number-average DP profile that is gained from intrinsic viscosity measurement. The depolymerization rate constant was obtained by fitting the model parameter by reducing sugar production results. Radical production was also presented to correlate the concentration of the radical to the sonication degradation ability. The amplitude of sonication is a controllable equipment parameter strongly related to how much energy is delivered. Hence, the variation of amplitude in this works is obliged to study the effect of energy delivered to starch degradation.

2. Process Model

Generally, a typical polymeric compound depolymerization model may be applied to this case: randomized chain scission and end-chain scission [9]. Fully randomized chain scission may be modeled as a probability term and provide fast chain length reduction [10]. End chain scission enables the process to produce a high yield of the monomeric compound but often resulted in a slower reaction [2].

Using the nth-order reaction, the number average molecular weight profile was obtained. This function will be correlated with classical depolymerization induced by radicals to predict the total monomer product. The equations are time dependent on the function of Number Average Molecular Weight (Mₙ, g/L) and monomeric material weight concentration (Cₛ, g/L). Number-average molecular weight is an important parameter that depicts the average chain length and easy to be measured. Much monomeric material can be produced throughout this process, such as glucose, fructose, maltose, and other reducing sugars can be estimated using the DNS method.

2.1. Number Average Molecular Weight from Ubbelohde Viscosimetry Data.

We developed the equation based nth-order reaction, which has been applied to other polysaccharide degradation using sonication [11]. The change in polymer molar concentration ([Mₚ]) was determined by the constant rate (k'), as shown in Eq. 1.

\[
\frac{d [M_p]}{dt} = k' [M_p]^n
\]  

(1)

Constant total weight of polymer solution (Wₚ) and time depended-number average molecular weight (Mₙ) are inscribed in Eq. 2:

\[
[M_p] = \frac{W_p}{M_n}
\]

(2)

Inserting Eq. 2 to Eq. 1 to obtain:

\[
\frac{d M_n}{dt} = k' W_p^{(n-1)} M_n^{(2-n)}
\]

(3)

These parameters (k', n) was obtained by parameter fitting using following intrinsic viscosities function that combined Mark Houwink Sakurada equation (Eq. 4) and n-order depolymerization reaction according to Li et al. [11] as depicted in Eq. 5-6.

\[
[\eta] = K M_n^{\beta}
\]

(4)
\[ [\eta]_t = \left( (1 - n)k'' t + [\eta]_0 \right)^{(n-1)/\alpha} \]  
\[ k' = k''(K [(1 + \alpha)\Gamma(1 + \alpha) W_p^{\alpha(1-n)/\alpha} \]  

2.2. Glucose Production Prediction using the Free-radical Degradation Model.

The equation was generated from initiation, propagation, transfer, and termination of radicals, as shown in Fig. 1. The equation was first proposed by Robert Simha and successfully simulated the radical degradation of several polymeric compounds in pyrolysis. Two parameters (\( \sigma \) and \( \varepsilon \)) were introduced to measure the radicals transfer effectivity, as shown in Eq. 7-8.

\[ \left( \frac{1}{\varepsilon} - 1 \right) = \frac{\text{propagation}}{\text{transfer+termination}} = \text{number of zip length} \]  
\[ \sigma = \frac{\text{transfer}}{\text{initiation}} = \text{transfer ratio} \]  

Near zero value of \( \sigma \) means, the mechanism approximated chain-end only because of only a small radical transfer. Term "zip length" describes radicals' propagation compared to the sum of transfer and termination. Small value zip length will need \( \varepsilon \) value near one that implied a random scission point mechanism. The general expression was written in Eq. 9.

\[ \frac{dC_S}{dt} = \frac{A-B}{E} \]  
\[ A = 2k_{dp} \left[ \frac{1}{\varepsilon} + \sigma + \left( \frac{1}{\varepsilon} \right) P + \left( \frac{1}{\varepsilon} \right) \right] (1 - C_S) \]  
\[ B = 2 \left( \frac{1}{\varepsilon} - 2 \right) \left( \frac{1-C_S}{P} \right) \frac{dP}{dt} \]  
\[ E = \left[ 1 + \frac{2}{P} \left( \frac{1}{\varepsilon} - 2 \right) \right] \]  

The average degree of depolymerization (\( \bar{P} \)) as the number average molecular weight (\( M_n \)) divided D-glucose Molecular Weight (\( MW_{DG} \)).
\[ \bar{p} = \frac{M_n}{MW_{DG}} \]  

(10).

2.3. Bubble Dynamics with Radical Production Model in Starch-Water Suspension

2.3.1. Bubble Dynamics. The single bubble sonochemistry model adopted the Keller-miskis equation (Eq. 11-13) with the first-order term in Mach number (\( M = \frac{R}{c} \)) that have been fully described in other research [12]. The ideal gas rule follows temperature and pressure. The equation correlated single bubble compression cycle through the bubble pressure (\( p_b \)) balance that induced by acoustic pressure. The expansion of the bubble is considered isothermal, and its total compression is followed by an adiabatic term (Eq. 4).

\[ (1 - \frac{R}{c}) \frac{R}{c} \frac{\partial R}{dt} + \frac{3}{2} \frac{R}{c} \frac{\partial R}{dt} = \frac{1}{\rho_0} \left( 1 + \frac{R}{c} \right) p_w + \frac{R}{\rho_0 c} \frac{dp_w}{dt} \]  

(11)

\[ p_w = \left( p_0 + \frac{2\sigma}{R_0} \right) R_0 \frac{3}{2} \frac{R}{c} \frac{\partial R}{dt} - \frac{2\sigma R}{R^2} - \frac{4\mu R}{R^2} \]  

(12)

\[ \frac{dp_w}{dt} = \left( p_0 + \frac{2\sigma}{R_0} \right) \frac{\gamma}{\rho_0} \left( \frac{R_0}{R} \right)^{3(\gamma-1)} \left( -3 \frac{\dot{R}}{R_0} \frac{3}{2} \frac{R}{c} \frac{\partial R}{dt} - \frac{2\sigma R}{R^2} - \frac{4\mu R}{R^2} - \left( -P_A \left( 2\pi f \right) \cos \left( 2\pi f t \right) \right) \right) \]  

(13)

In this equation (Eq. 11-13), dots showed time derivative (\( d/dt \)), \( R \) is the radius of a bubble, \( c \) is the speed of sound, \( \rho_0 \) is bulk density, \( \sigma \) is surface tension, \( \gamma \) is Laplace constant, \( P_A \) is acoustic amplitude, \( f \) is frequency velocity. Acoustic pressure depended on acoustic intensity as Eq. 14. The acoustic intensity can be measured as the energy dissipated in a cross-sectional area (\( I_a = \frac{1}{A_{cs}} \frac{dE}{dt} \)). An alternative way to measure the actual acoustic intensity was depicted by Sathiskumar and Madras [13], which use calorimetry. By measuring bulk temperature, the intensity can be written as Eq. 15. The cross-sectional area \( A_{cs} \) was sonotrode surface area.

\[ P_A = (2 I_a \rho_1 c)^{1/2} \]  

(14)

\[ I_a = \frac{m c_p d T_L}{A_{cs} dt} \]  

(15)

2.3.1. Radical Reaction. Chemical kinetics model and reaction constant was simulated followed the series radical formation reaction by Merouani et al. [14]. The reaction equation is considered a reversible elementary reaction in bubble thin film with bubble temperature (\( T_b \)) followed Eq. 16-19. Reaction rates (\( r \)) was the function

\[ T_b = T_L \left( \frac{R_0}{R} \right)^{3(\gamma-1)} \]  

(16)

\[ \Sigma_{k=1}^K v_{ki} X_k \rightleftharpoons \Sigma_{k=1}^K v_{ki} X_k \]  

(17)

\[ \dot{w}_k = \Sigma_{l=1}^l (v_{kl} - v_{kl}) r_l \]  

(18)

\[ r_i = k_{fi} \prod_{k=1}^K [X_k]^{v_{ki}} \]  

(19)

3. Method

3.1. Experimental

Cassava starch was a commercial-grade from Budi Jaya (Jakarta, Indonesia). Potassium hydroxide (1310-58-3), sodium hydroxide (1310-73-2), potassium iodide (7681-11-0), and perchloric acid 70% (7601-90-3) were obtained from SAP Chemical (Jakarta, Indonesia). Potassium sodium tartrate (6381-
59.5/108087) and anthrone reagent (90.44–8/101468) and were purchased from Merck (Darmstadt, Germany).

Sonication was conducted as previous work [15]. The aqueous starch mixture was made by mixing 5 g starch in 100 mL distilled water. Sonication was carried out under various amplitudes for 60 min, and the bulk liquid temperature was recorded. The variable was listed in Table 1.

### Table 1 List of variables and amplitude used.

| Name | The percentage from the maximum amplitude (%) | Ideal Equipment Amplitude (μm) |
|------|---------------------------------------------|--------------------------------|
| S30  | 30                                          | 34.2                           |
| S40  | 40                                          | 45.6                           |
| S50  | 50                                          | 57.0                           |
| S60  | 60                                          | 68.4                           |
| S70  | 70                                          | 79.8                           |

### 3.2. Chemical Analysis

#### 3.2.1. Ubbelohde Viscosimetry. The intrinsic viscosities of the measurement method was based on another experiment [16]. $M_v$ was calculated by Mark Houwink equation for amylose of starch (Eq. 4), taking $'K'$ as 0.00183 and 'a' as 0.89 [17]. Solutions were prepared with a sample concentration of 0.1%–0.4% in 1 M potassium hydroxide. It was filtered, and the viscosity was measured using Schott-Gerate Ubbelohde Capillary Viscometer Model 525 (Darmstadt, Germany). The measurement was repeated at least three times.

#### 3.2.2. Total Reducing Sugar for DNS Method. The liquid product was analyzed using the DNS method. The method was adopted from elsewhere [18]. The standard solutions were made from D-glucose solution. The spectrophotometry was conducted at 502 nm wavelength (Genesys 10S UV-Vis spectrophotometer).

### 3.3. Simulation

The constant was adapted from other experiments, as listed in Table 2. The constant density of 1050 kg/m³ applied in this work was obtained from the experiment. The bubble dynamic and chemical reaction equations solved simultaneously using the ODE package of MATLAB 2020 (academic version). The fitting parameter was done by evaluating the parameter value to non-linear least square regression.

$$s^2 = \sum_i^n \frac{(y_i - y_{exp})^2}{N-K}$$

(20)

### Table 2 List of constant used in the bubble dynamic equation.

| Symbol | Unit     | Value                                           | Ref.     |
|--------|----------|-------------------------------------------------|----------|
| $\gamma$ | $4/3$    |                                                 | [19]     |
| $M$    | Pa s     | $124.68 - 0.36T_L$                              | [20]     |
| $p_0$  | Pa       | $1.013250 \times 10^5$                         | [21]     |
| $c_p$  | J/g C    | $4.70518 + (-3.71017)X_s + 0.00343 (T_L - 273) + 3.24167 (X_s^2) + (-2 \times 10^{-4})(T_L - 273)^2$ | [22]     |
| $\sigma$ | N/m     | 0.078                                           | [23]     |
| $p_v$  | Pa       | $133.32 \exp \left(18.3036 - \frac{381.644}{T_L - 46.13} \right)$ | [21]     |
4. Results and Discussion

The Sonication process induces starch degradation by microjet and radicals. The microjet eroded the granule and detached the starch molecule. The radicals contacted a free starch molecule, therefore made charge destabilization of an oxygen atom at glycosidic bond [7]. This effect is shown by depolymerization kinetics, which combined the n-th order reaction and free radical degradation model.

4.1. Depolymerization Kinetics

The number average molecular weight and total reducing sugar data were utilized to obtained 5 equation constant listed in Table 3. Firstly, the determination of $k''$ and $n$ were derived from the correlation between the intrinsic viscosities measurement and the n-order reaction kinetics equation. The value of $k_{dp}$, $\sigma$, and $\varepsilon$ were obtained from the fitting between total reducing sugar (monomer) concentration profile and free radical depolymerization equation.

| Variable | $k_{dp} \times 10^6$ | $\sigma$ | $\varepsilon$ | $k'' \times 10^{13}$ | $n$ |
|----------|----------------------|---------|--------------|-------------------|------|
| S30      | 61                   | 0.9     | 1.0          | 7.1               | -3.2 |
| S40      | 85                   | 0.1     | 1.0          | 6                 | -3.2 |
| S50      | 8.5                  | 1.0     | 0.6          | 30.1              | -3.2 |
| S60      | 12                   | 0.6     | 0.5          | 7.1               | -3.2 |
| S70      | 8.5                  | 0.1     | 0.1          | 48                | -3.2 |

The intrinsic viscosities profile and average molecular weight were presented in Fig. 2. The sonication reduced a high amount of starch molecule chain early. Sonication delivered immense energy intensity, inducing cavitation that made the sonication have the ability to degrade chemically by radicals and physically by microjet [3,24]. The result shows that the process has negative value of reaction order ($n$), which can be classified as physical process control. This negative value of reaction order also means that increase of polymer concentration made the reaction rate decrease [25]. This also implied that the chemical degradation was much faster than the physical degradation so that the average process can be considered physical process control.

Besides, the higher bulk temperature will trigger the starch granule to be gelatinized. The amount of water penetrated inside the granule matrices as the intermolecular bond of starch weakened. It decreased the total amount of free water in bulk liquid; therefore, the viscosity increase. A more viscous solution may retard the microjet power that hit starch granules.
The monomeric product of the starch depolymerization process can be predicted as reducing sugar production depicted in Fig. 3. It is found that the calculated concentration of reducing sugar tends to increase over the processing time. However, the experimental results show a fluctuating trend over time with a maximum yield of reducing sugar of 0.570 g / L in the process using S30 for 60 minutes. From the graph, the value of apparent reaction rates may appear in sequence from S30>S40>S70>S60>S50. Practically, it is agreed that the fluctuating monomer production may come from radicals based degradation. Radicals tend to have a random scissoring point, which hard to be stable. This semi-empirical model may help the rough prediction of monomer production from the starch sonication process.

4.2. Radical Production from Acoustic Cavitation in Starch-Water Suspension

Bulk liquid temperature profile from experimental data was converted to calculated dissipated energy used in radical production prediction. The cavitation comes from high-intensity acoustic pressure caused by an extreme compression-rarefaction cycle to generate a local hotspot. The cavitation bubble's
Implosion made the liquid contacted the local hotspot, then raise the bulk liquid temperature. From Fig. 4, the higher amplitude achieved higher stability at about 12 minutes process that may occur by a steady-state between heat generation by cavitation and heat dissipation. Higher amplitude means that higher acoustic pressure was applied to the bulk liquid, resulting in a high compression ratio from the cavitation bubble. It generates a local hotspot with high local pressure and temperature, resulting in higher heat generation from the process.

![Temperature profile of the starch sonication process.](image)

**Figure 4** Temperature profile of the starch sonication process.

The bubble dynamics of sonication is presented in Fig. 5. This result was different from sonication in constant bulk temperature pure water [14], which demonstrated a high bubble maximum compression ratio. It was expected that cavitation in aqueous starch solution showed milder cavitation than it is in pure water due to the bubble growth strongly inhibition by high density and surface tension. It is also found that a higher amplitude corresponded to a higher maximum bubble radius. The sonication wave's oscillatory pattern made a high amplitude to have high positive and high negative acoustic pressure; therefore, it can result in a higher bubble radius. As the bulk temperature rises at a more prolonged process time, the speed of sound was reduced. Lower speed of sound makes a lower the sound intensity to decrease the maximum acoustic pressure.
Radicals may be produced because the water components (water molecule and dissolved gases (H$_2$ and O$_2$)) create contact with the local hotspot [21]. The local hotspot's high temperature opens the possibilities to the water components take a sudden molecular cleavage that can occur at the thin bubble film layer. The predicted maximum of three radical products (H*, OH*, and HO$_2$*) is presented in Fig. 6. The maximum value of H* concentration was 0.00278 M, which was obtained from S30. It is also found that the OH* concentration was reached its maximum value at S70 (0.01051 M). S50 produced the most HO$_2$* with a value of 2.29957 x 10$^{-13}$ M. Generally, H* showed values more than 0.00012 M. Meanwhile, OH* have concentration below 1.2 x 10$^{-5}$ M, except S70 which show the highest value among the radicals. It is also showed that the HO$_2$* value was below 2.5 x 10$^{-13}$ M.
Figure 6 Maximum radicals (H*, OH* and HO$_2^*$) concentration formed in the bubble wall from starch sonication process.

The contribution of the product of each radical to the degradation of starch is still much debate. From the value of radical concentration, H* and OH* may be positioned to have the most significant effect among the radicals. Further evidence showed that the highest apparent reaction rates correlate with the highest H* concentration (S30), and the second-highest apparent reaction rates correlate with the highest OH* concentration (S70). From this result, further work may be focused on the total of H* and OH* to be applied in the radical-dependent reaction rate for the depolymerization model.

5. Conclusion
The experimental and simulation of the starch sonication process has been done in this work. The experimental result shows fluctuating trend monomer production over time with a maximum yield of reducing sugar of 0.570 g / L in the process using S30 for 60 minutes. The free-radical degradation model can be a rough prediction of monomer production from the starch sonication process. The bubble dynamics simulation has been done with the Keller-Miskis equation. The highest value of H*, OH*, and HO$_2^*$ is 0.00278 M, 0.01051 M, and $2.29957 \times 10^{-13}$ M, respectively. The highest apparent reaction rate of the free-radical degradation model correlates well with the highest H* concentration depicted by the S30 process.

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