Experimental and Numerical Simulation of Starch Degradation under Sonication Process

D W Andriansyah, A A Billah Al-Firdaus, B Airlangga, P N Trisanti, Juwari, Sumarno

1 Student, Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, Surabaya, Jawa Timur 60111, Indonesia
2 Lecturer, Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, Surabaya, Jawa Timur 60111, Indonesia

Corresponding Author’s e-mail: onramus@chem-eng.its.ac.id

Abstract. Starch processing technology has been developed to enlarge the application of starch in most of food, medical and fermentation industries. Sonication is prominent technology that can alter physical and molecular structure of many material by generating vigorous cavitation which gives radicals and a microjet. Many researches of starch sonication process has been carried out experimentally, but there is only very small number of published works that correlated the experiment data and suitable reaction model. In this study, a reaction model that correlates with experimental results was develop to predict molecular weight, granule size, and conversion of cassava starch. The sonication has simulated with the n-th-order reaction model. The result show the reaction was controlled by physical process control. The simulation depict that sonication process can produce a lower molecular weight of starch in very short time. At later time process, the sonication degradation ability was reduced because some part of granule have ability to withstand the cavitation.

1. Introduction
Starch is a natural polymer that can be found in stems (sago), leaves (plants), roots (tubers), fruit (lindur fruit), and other plant parts. It is produced by utilizing solar energy through photosynthesis process. In the photosynthesis process, plants will produce carbohydrates from carbon dioxide and mineral substances that are absorbed by plants. The starch will be stored in food reserve storage organs such as tubers, fruit and seeds [1]. Through degradation process to lower molecular weight compounds, starch can enlarge its function as raw material for bioethanol, adhesive, pharmaceutical and other food industries. In Indonesia, bioethanol is considered as one of the renewable energy sources that are being produced rapidly.

Bioethanol can be produced through the fermentation process of glucose that can be derived from breaking starch molecule. The development of starch degradation process method to produce glucose or other reducing sugar has begin since early of 1800 using hot-concentrated acid process [2]. Nowadays, more eco-friendly and clean process has been taken huge attention by reasearchers.

Ultrasound, one of fascinated method in starch processing, uses ultrasonic waves generated from a sonication probe. The probe produce waves with frequencies between 20 kHz to 10 MHz. The ultrasonic waves generate acoustic cavitation which results in rapid bubble formation. The bubble
growth by intensive compression-rarefaction cycle henceforth lead the bubbles collapse with a high local temperature (up to 5000 K) and a high pressure (up to 20 MPa) [3]. As the bubble collapse with such energy, radicals and microjet can be produced, therefore the sonication may have high degradation ability in aqueous mixture of many compounds [4]. When ultrasound occurs in aqueous suspension of starch, ultrasound can perform chemical bonds breaking which results in the formation of low molecular weight starch and reducing sugars [5].

Despite of many sonication experiments of starch degradation has been conducted [6–8], there are not much reasearch focused on finding process model simulation which correlate to experimental result. Therefore, this work was set out to develop the n-order depolymerization reaction equation to be correalted to experimental result. The experiment was conducted by processing aqueous starch suspension using horn-type sonication. Intrinsic viscosity was measured in order to obtain reaction constant. To correlate the depolymerization process with the carbohydrate fraction, anthrone method was used to obtain the carbohydrate fraction.

2. Experimental

2.1. Materials
Cassava starch was commercial grade from Budi Jaya (Jakarta, Indonesia). Sulfuric acid 98% (7664-93-9), Ethanol 96% (64-17-5), 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).

2.2. Sonication Treatment
In this work, a 500 W horn-type sonication probe was operate with 100 mL aqueous cassava starch suspension (5% g/mL). The sonication treatment steps was detailed in the previous work [9]. Ideal amplitude of 36.48 μm and frequency of 20 kHz.

2.3. Number Average-molecular weight of Starch
Number-average molecular weight ($M_n$) was correlated by viscosity-average molecular weight as amylose ($M_v$) using equation (1).

$$M_n = \frac{M_v}{\Gamma(1 + \alpha)}$$

Ubbelohde Viscosimetry method, which was used to determine the $M_v$, was adapted from other experiment [10]. Mark-Houwink Sakura da equation was used as equation (2) with taking K and α from other experiment [11].

$$[\eta] = KM_v^\alpha$$

2.4. Carbohydrate Fraction of Starch Granule
Carbohydrate fraction of the starch granule was done using Anthrone which described elsewhere [12]. The standard curve was calibrated using D-glucose. The reagent was prepared in the same day as measurement time. Carbohydrate fraction is determined by equation (3).

$$X = 1 - x_i/x_o$$

Where X is the conversion of starch, $x_i$ is the final fraction, and $x_o$ is the initial fraction.
3. Simulation

3.1. Process model

The process model was composed of (a) starch molecule detachment from its granule form by microjet and (b) starch molecule cleavage by radicals. We developed the equation based $n$th-order reaction which has been applied other polysaccharide degradation using sonication [13]. The change of polymer molar concentration ($[M_P]$) was determined by constant rate ($k'$) as shown in equation (4).

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

(4)

Constant total weight of polymer solution ($W_P$) and time depended-number average molecular weight ($M_n$) are inscribed in equation (5):

$$[M_P] = \frac{W_P}{M_n}$$

(5)

Inserting equation (4) to equation (5) to obtain:

$$\frac{dM_n}{dt} = k'W_p^{(n-1)}M_n^{(2-n)}$$

(6)

Combined Mark-Houwink Sakurada equation (equation (2)) and n-order depolymerization reaction according Li et al [13] as depicted in equation (7) and equation (8).

$$[\eta] = \left( (1 - n)k'' t + [\eta]_0 \right)^{(n-1)/\alpha}$$

(7)

$$k' = k''(K [(1 + \alpha)\Gamma(1 + \alpha)] W_p^\alpha)^{(1-n)/\alpha}$$

(8)

The starch granule conversion was estimated to correlate with the carbohydrate conversion. It was adapted from the the Einstein equation and viscometric data to estimate the volume of polymer [14].

$$V_\eta = \frac{2 M_n [\eta]}{5 N_A}$$

(9)

The granule conversion ($X_{SG}$) was calculated as solid particle conversion

$$X_{SG} = 1 - \frac{V_\eta(t)}{V_\eta(0)}$$

(10)
3.2. Process parameter

To obtain reaction constant \((k', n)\), fitting parameter was done by evaluating the parameter value to non-linear least square regression [15]. The calculation and the lowest error was obtained by Matlab 2020 (Academic version).

\[
\sigma = \frac{S^2}{N - K} = \sum_{i=1}^{N} \left( \frac{[\eta]_{t,im} - [\eta]_{t,ic}}{N - K} \right)^2
\]

(11)

Where:
- \(S^2\) = \(\sum (r_{im} - r_{ic})^2\)
- \(N\) = Total run
- \(K\) = The number of parameters to be specified
- \([\eta]_{t,im}\) = Measured intrinsic viscosities
- \([\eta]_{t,ic}\) = Calculated intrinsic viscosities from equation (7)

4. Results and Discussion

4.1. Fitted parameter

The least square analysis method is used to determine the \(k''\) and \(n^{th}\)-order reaction in equation (7). The squared difference (\(\sigma\)) over the parameter is shown in figure 1. The calculation result in the lowest \(\sigma\) value is obtained at \(k'' = 8.6 \times 10^{-14}\) and the \(n\) is -3.6. This negative value of the order reaction was is agreed with other sonication process of polysaccharide compound [16].

![Figure 1. Fitting reaction rate constants \((k'')\) and \(n^{th}\)-order reaction from sonication process.](image)

Intrinsic viscosities is a kind of viscosities that represent the single molecule viscosity, so that can correlate to molecular weight of polymer. The obtained value constant \((k''\) and \(n)\) is simulated to show the intrinsic viscosities profile as shown in figure 2. The sonication reduced a high amount of starch molecule chain at early time. Similar pattern also has been found in xanthan gum degradation using sonication [17]. Sonication deliver huge intensity of energy, inducing cavitation that made the sonication have ability to degrade chemically by radicals and physically by microjet. From the result, it is found 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 [16]. This also implied the chemical degradation was much faster than the physical degradation so that the average process can be considered as physical process control.
4.2. Number average molecular weight

The number average molecular weight ($M_n$) was estimated as shown in figure 3. It shows a similar pattern with the intrinsic viscosities profile (figure 2). It also found that the initial average molecular weight was $9 \times 10^5$ Da. It is important to note that starch have amylase ($M_w = 10^5-10^6$) and amylpectin ($M_w = 10^7-10^8$) as its major component. It may be possible that its mixture may have average value around the obtained value. The molecular weight profile was decreased significantly at very short early time. Later, the $M_n$ was show value around $1 \times 10^5$ Da.

![Figure 2. Simulation (line) and experimental result (dot) from sonication process.](image)

![Figure 3. Number average molecular weight change over time.](image)

The starch polysaccharide chain at the beginning of time is very complex and long, therefore at the beginning of time it shows a very large decreasing graph because sonication works effectively at the beginning of time in cutting the polysaccharide chain. However, as the sonication process progresses, the polysaccharide chains become shorter and stiffer, so the microjet effect becomes less effective at the end of time. It can be seen that these results suggest the importance of molecular interactions and should not be neglected when the molecular chains are long and tend to form entangled structures. Conversely, after sonication, the molecular chains become shorter and stiffer, the effect of molecular interactions on molecular viscosity becomes smaller.

In addition, higher bulk temperature and shear force from microjet will trigger the starch granule to be gelatinized [18]. Amount of water penetrated inside the granule matrices as the intermolecular bond of starch weakened. It decrease the total amount of free water in bulk liquid, therefore the bulk
viscosity increase. More viscous solution may retard the microjet power to hit starch granules. In polymer degradation term, scission of a polysaccharide chain can produce some shorter polysaccharide before it produce some oligosaccharides and monosaccharides substance.

4.3. Carbohydrate fraction of starch granule

Carbohydrate conversion (X) is amount of carbohydrate that converted to oligosaccharide or low molecular weight polysaccharide. Experimentally, it measured by anthrone method which is shown as dot plot in figure 4. Line plot also show the prediction of granule conversion which related to molecular weight using equation (9) and equation (10). It is found that the estimation still overpredicted related to experimental result.

![Figure 4. Conversion of Starch from sonication process of cassava starch.](image)

The overpredicted calculation happen because starch granules have a various shape and size as well as chains of starch which are branched and linear. The contribution of semicrystalline structure was attributed to the overestimation of the conversion.

5. Conclusion

The starch degradation has been simulated using n-th order depolymerization reaction kinetics. The intrinsic viscosities was in line with experimental result. It is also found that the sonication can reduce the number molecular weight from 9x10^5 Da to about 1x10^5 Da. Prediction of carbohydrate granule conversion using Einstein Particle Volume and Empirical Radius of Gyration is still give higher result than experimental result. It is necessary to develop a model for conversion because the results obtained are still not in accordance with the experimental results.
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Acknowledgments

The authors thank to the Ministry of Research, Technology, and Higher Education of Indonesia. This study was financially supported by the PMDSU Scholarship Program and PKM Program.