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EFFECT OF ULTRASOUND ON SULFURIC ACID-CATALYSED HYDROLYSIS OF STARCH

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Abstract—The influence of ultrasound on the hydrolysis of starch was investigated at moderate temperature range (90-100℃) and in the dilute sulfuric acid (1-5 wt%). Enhancements of the reaction rate by ultrasound was observed. The degree of the relative enhancement depended on the reaction temperature. The model reaction by maltose showed that the acid hydrolysis of glucosidic linkages was first order with respect to the substance concentration and the hydrogen ion concentration, respectively. And the activation energies of the control and the ultrasound-aided hydrolysis of maltose were 30.2 and 23.4 kcal/mol, respectively. Enhancement was thus expressed as the alleviation of activation energy by ultrasound irradiation.

INTRODUCTION

Starch consists of glucose, as the monomeric building unit, which is a raw material for other chemicals. Among many uses of glucose, some interests have been focussed on the formation of ethanol from fermentation. Ethanol can be replaced with fossil-based liquid fuels as a blend with gasoline and also can be catalytically dehydrated to ethylene or higher hydrocarbons.

Acid hydrolysis aims the mass production of fermentable sugar from starch. Two main developing or commercialized acid hydrolysis processes of starch; Dilute Acid Hydrolysis Process (DAHP) and Concentrated Acid Hydrolysis Process (CAHP) have been introduced. CAHP is operated at the condition of high acid concentration (above 1 M HCl) and at low temperature (below 70℃), which takes a long reaction time [1]. The neutralization and the separation of acid are the main problems in CAHP. DAHP is carried out in a few second or minute at high temperature (between 150 and 200℃) and dilute acid (below 3 wt%) [2-6]. DAHP involves the undesired by-products from degradation, reversion and retrogradation while it has some merits on the hydrolysis rate and the alleviation of the neutralization. Starch hydrolysis has been also performed at moderate temperature between 90 and 120℃ for analytical application. This takes about 3 hr to complete the reaction in the case of 0.7 M HCl [7-9].

Efforts to develop more suitable hydrolysis process at relatively low temperature and dilute acid have been studied. The rate enhancement by ultrasound is one of them. It was reported that acid hydrolysis of methyl acetate [10], dextran [11, 12], and sugar cane bagasse [13] were promoted by ultrasound. In the present study, we investigated the effects of ultrasound irradiation on sulphuric acid-catalysed hydrolysis of starch. Maltose hydrolysis was chosen as a model reaction to study the promotion effect in the hydrolysis of glucosidic-bonded polymers.

EXPERIMENTAL

The hydrolysis apparatus shown in Fig. 1 consists of an ultrasound generator (25 KHz, 600 W) and a pyrex reactor (150 ml). The reactor contacting the ultrasound concentrator was sealed by a viton O-ring. The inside temperature of the reactor was measured and controlled.

An aqueous solution of starch was charged to the reactor, being agitated with a magnetic bar, preheated up to the reaction temperature, and followed by the addition of the acid with a syringe when temperature was stable. The ultrasound was irradiated continuously during the reaction. The control hydrolysis was also run under the identical conditions in the absence of the ultrasound.

Samples were suctioned through a teflon tube (2 mm OD) with a syringe after given interval, cooled

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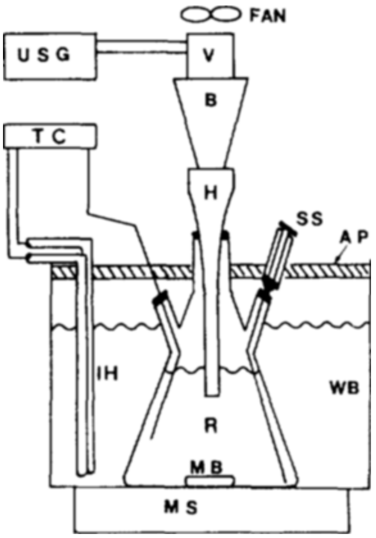


Fig. 1. The hydrolysis apparatus with ultrasound.

B: Booster horn
H: Exponential concentrator
R: Reactor
V: BLT Vibrator
SS: Sampling syringe
USG: Ultra sound generator
AP: Asbestos sheet
IH: Immersed heater
MB: Magnetic bar
MS: Magnetic stirrer
TC: Temperature controller
WB: Water bath

immediately at the room temperature, and neutralized with barium hydroxide. The neutralized sample was centrifuged first at 3,000 rpm and secondly at 15,000 rpm. Samples were separated through a Bio-Rad Q 153 ion resin column at 83℃. Oligomers, maltoriose, maltose, and glucose were detected by a refractometer. And hydroxymethyl furfural (HMF) was detected by an UV detector.

Starch from maize (Fluka Bio Chemika, $M_w=13{,}000$, $M_n=3{,}000$, and more than 80%), D-(+)-maltose monohydrate (Janssen Chimica, 93%), sulphuric acid (Matsunoen Chemical Co., 97%), and barium hydroxide (Shinyo Pure Chemicals Co., Ltd., 97%) were used in the experiment.

RESULTS AND DISCUSSION

1. Temperature Programmed Hydrolysis of Starch

In order to investigate the degradation of starch hydrolysates temperature programmed hydrolysis was carried out in an autoclave (Parr model 4563; 600 ml). The reaction temperature of the closed vessel was smoothly increased up to 160℃ as shown in Fig. 2. Fig. 2 shows glucose was produced above 100℃. Maltose and maltotriose were coproduced with glucose The formation of HMF from the dehydration of glucose indicated the presence of side reaction. This side reaction occurred at a temperature above 150℃. HMF was detected within a few minutes at 160℃. Table 1 shows the maximum yield of glucose (Y_G) without accompanying the formation of HMF, where Y_G is G/S_0 multiplied by 100, G is the weight percent (wt%) of glucose produced, and S_0 is the initial wt% of starch. The maximum yield of glucose without considering by-products was about 63% and occured at the acid concentration between 0.3 and 0.5 wt% at 160℃. The degradation of glucose occurred more rapidly at higher acid concentration. Assasson et al. [4] reported that 73% dextrose equivalance was achieved with the accompany of 4% gentiobiose as by-product at 167℃.

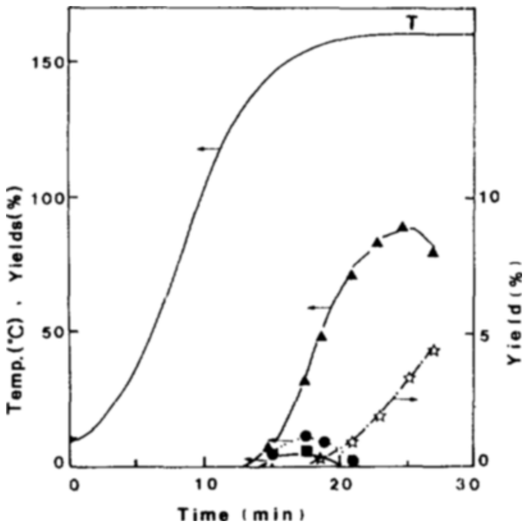


Fig. 2. Product yields from the temperature programmed hydrolysis of starch (5 wt% starch, 0.3 wt% H_2SO_4); ▲ glucose, ● maltose, ■ maltotriose, ☆ HMF.

Table 1. The maximum yield of glucose without by-products in the temperature programmed reaction

H_2SO_4 concentration (wt%)	Temperature (℃)	Pressure (bar)	Glucose yield (%)
0.15	160	5.2	47
0.3	159	5.1	63
0.5	156	4.7	62
0.7	145	3.3	54

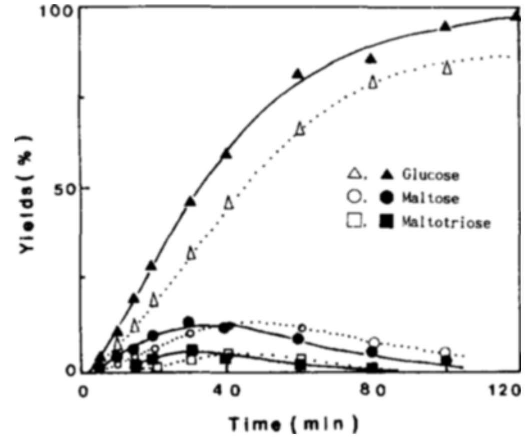


Fig. 3. Product distribution of sulfuric acid hydrolysis of starch with (solid line) and without (broken line) ultrasound, respectively, at 100°C; 3 wt% starch and 5 wt% H_2SO_4.

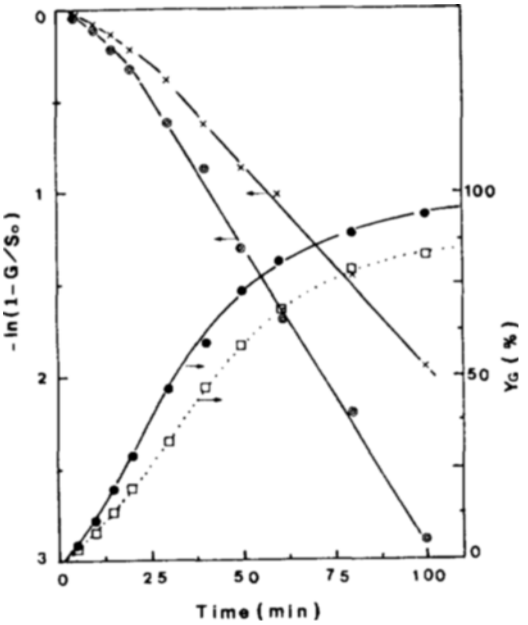


Fig. 4. The promotion effect by ultrasound on the glucose yield and the plot of ln $(1-G/S_o)$ vs. time on the starch hydrolysis at 100°C (3 wt% starch, 5 wt% H_2SO_4); ×, ● for with ultrasound (W/US) and ◎, □ for without ultrasound (WO/US).

The acid hydrolysis of the general semi-commercial processes [4-6] was completed in a few minutes at a temperature below 200℃, at less than 0.3% acid concentration, and at 30-60 bar.

Table 2. The relative enhancements by ultrasound on the glucose yield from the starch hydrolysis

Temperature (℃)	H_2SO_4 conc. (wt%)	Glucose yield(%) Y_G^U	Glucose yield(%) Y_G^C	Relative enhancement (%)[a]
100	5	81.0	66.3	22.1
95	5	53.7	42.9	25.3
90	5	36.3	18.1	100.3
100	3	49.4	37.8	30.8
95	3	32.1	17.9	78.9
100	1	36.0	26.4	36.4

[a] Relative enhancement was defined as $(Y_G^U-Y_G^C)/Y_G^C$.

Our interests are the promotion of the glucose yield without by-products with dilute acid. It was recommended from our experimental results that the hydrolysis should be performed at a temperature below 160℃ in order to prevent the formation of by-products. Ultrasound was chosen to promote the hydrolysis at low temperature.

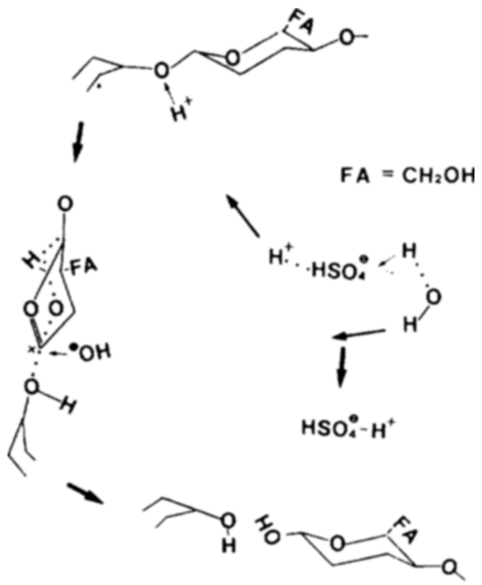
2. The Effect of Ultrasound on the Starch Hydrolysis

The typical product distribution from the starch hydrolysis is shown in Fig. 3. Maltose and maltotriose was coproduced with glucose from the initial stage in both cases of with and without ultrasound. This means that a random scission of the glucosidic linkages occurs during acid hydrolysis of starch [11]. Ultrasound shortened the time for the maximum production of maltose and maltotriose from 42 to 38 minutes.

Fig. 4 shows a typical trend of the rate enhancement by the ultrasound irradiation. The yield of glucose with ultrasound irradiation was dominant over the control reaction without ultrasound.

The relative enhancement of glucose formation from the starch hydrolysis was measured when the reaction proceeded for 60 minutes. Table 2 shows the glucose yields (Y_G^U and Y_G^C: superscripts U and C represent the ultrasound-aided and the control hydrolysis, respectively) and the relative enhancement. The relative enhancement was about 75% at 90℃, but decreased as the temperature increased. The temperature dependence on the relative enhancement was discussed in maltose hydrolysis.

The plot of $\ln(1-G/S_o)$ vs. time in Fig. 4 represents the elemination of starch during the reaction assumed first order kinetics for glucose formation. Non-linearity in the whole region is due to the coproduction of reduced sugar in the random scission of starch. On this viewpoint starch as a reactant varies time to time. And there is no way to set the correct reactant. This situa-



SCHEME 1

tion give us a difficult problem to analysis the experimental results. So we chose maltose as a model sustance to investigate hydrolysis of glucosidic linkages.

3. Kinetics of Maltose Hydrolysis

The ultrasonic effects in the hydrolysis of glucosidic linkages was studied through the kinetics of maltose hydrolysis as a model material. Maltose hydrolysis in acid solution is given by the Eq. (1). The hydrolysis of glucosidic linkages involves protonation of the glucosidic oxygen [11] as shown in Scheme 1.

$$\text{Maltose(M)} + \text{Water(W)} + H^+ = 2\ \text{Glucose(G)} + H^+ \qquad (1)$$

The rate is given by the Eq. (2) from the assumption of the first order dependence with respect to all elements. Where M, W, G, and $[H^+]$ are concentrations of maltose, water, glucose, and hydrogen ion, respectively. And

$$-dM/dt = k^+\ M\ W\ [H^+] - k^-\ G^2\ [H^+] \qquad (2)$$

k^+ and k^- are the rate constants of the forward and the backward reaction, respectively. Eq. (2) is simplified to Eq. (3) if the reverse reaction is negligible,

$$-dM/dt = k\ M \qquad (3)$$

where k, apparant rate constant, is $k^+W[H^+]$. We express k with Eq. (4) involving Arrhenius' temperature dependence and acid concentration, where F is the frequency factor and E_a is the activation energy.

$$k = F\ W\ [H^+]\ \exp(-E_a/RT) \qquad (4)$$

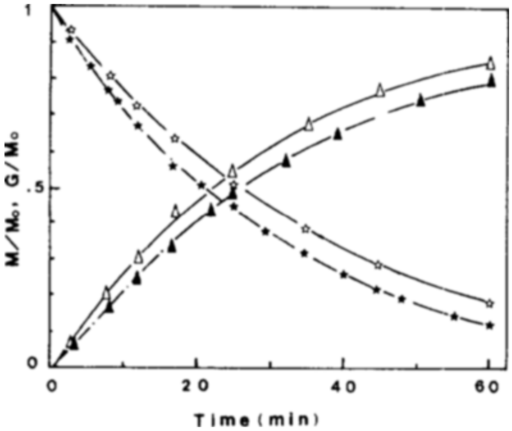


Fig. 5. The reduction of maltose (M/M_o; ☆ & ★) and glucose formation (G/M_o; △ & ▲) at 100°C (3 wt% starch, 3wt% H_2SO_4); with ultrasound (☆ and △) and without ultrasound (★ and ▲).

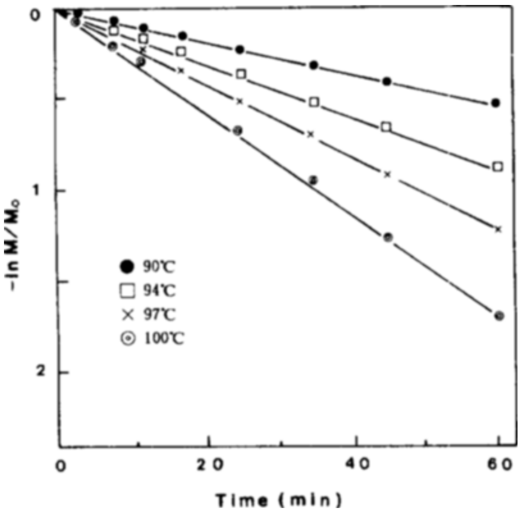


Fig. 6. Maltose reduction with time at the control hydrolysis (3wt% starch, 3 wt% H_2SO_4).

The integrated form of Eq. (3) is expressed with Eq. (5). This is the typical form of first order reaction with respect to a single component, where

$$\ln M/M_o = -k\ t \qquad (5)$$

M_o is the initial concentration of maltose. The typical trend of the maltose reduction and the glucose formation was shown at Fig. 5. It also shows the enhancement of maltose hydrolysis by ultrasound irradiation. The results were well fitted by Eq. (5) as shown at

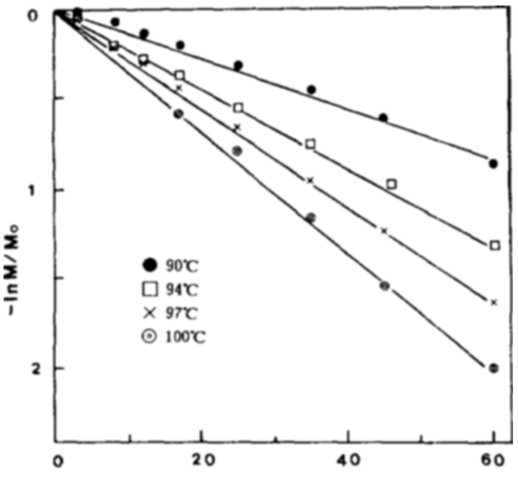


Fig. 7. Maltose reduction with time at the ultrasound-aided hydrolysis (3 wt% starch, 3 wt% H_2SO_4).

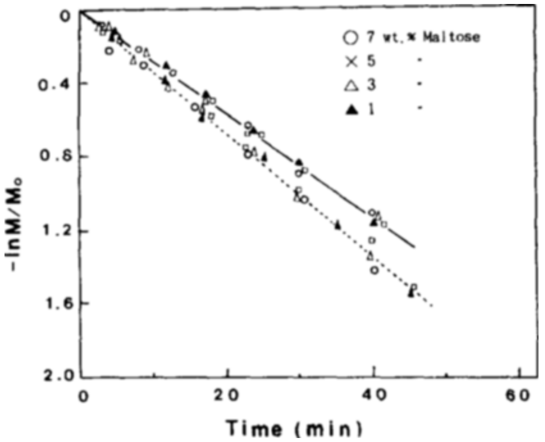


Fig. 8. The effect of maltose concentration on maltose hydroylsis with (broken line) and without (solid line) ultrasound, respectively, at 100°C and 3 wt% H_2SO_4.

Figs. 6 and 7, which implies that sulfuric acid- catalysed hydrolysis of maltose is first order to the maltose concentration. This first order reaction was also verified by the experimental results shown at Fig. 8 which show the kinetics was independent on the concentration of the initial glucose.

Fig. 9 shows the maltose hydrolysis was also well fitted with first order to H^+ concentration ($C_H{}^+$). And the power order expression of the rate constant with respect to $C_H{}^+$ gives unit value. $C_H{}^+$ of the dilute sulphuric acid was obtained from the data of Cox and Yates [16].

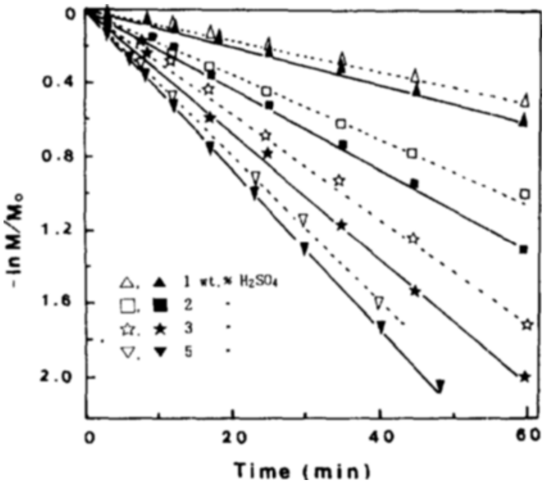


Fig. 9. The effects of acid concentration on the maltose hydrolysis with (solid line) and without (broken line) ultrasound, respectively, at 100°C and 3 wt% maltose.

Table 3. The relative enhancements by ultrasound in the maltose hydrolysis

Temperature (℃)	H_2SO_4 conc. (wt%)	Glucose yield(%) k^c	Glucose yield(%) k^u	Enhancement[a] (%)
100	1(0.1265)[b]	0.009	0.010	11.11
100	2(0.2472)	0.018	0.021	16.67
100	3(0.3698)	0.028	0.033	17.86
100	4(0.4955)	0.039	0.043	10.26
90	3	0.009	0.014	55.56
94	3	0.015	0.022	46.67
97	3	0.021	0.027	28.56

[a] Defined as $(k^u-k^c)/k^c$. [b] Parenthesis represents $C_H{}^+$ from the literature [16].

The observed rate constants and the relative enhancement were summerized in Table 3. The relative enhancement has a maximum value at the concentration of sulfuric acid between 2 and 3 wt% which are correspondent to 0.4 and 0.6 N H_2SO_4. The relative enhancement of rate constant was decreased as the temperature increased, which is the same as the case of starch hydrolysis. The relative decrease in ultrasound effect at high temperature will be due to the lower of cavitational collapses [17]. This temperature effects were negligible at a temperature below 80℃ for the case of polymer degradation [17], acid hydrolysis of dextran [12], and acid hydrolysis of methyl acetate [10]. Penthrick [17] also showed that the

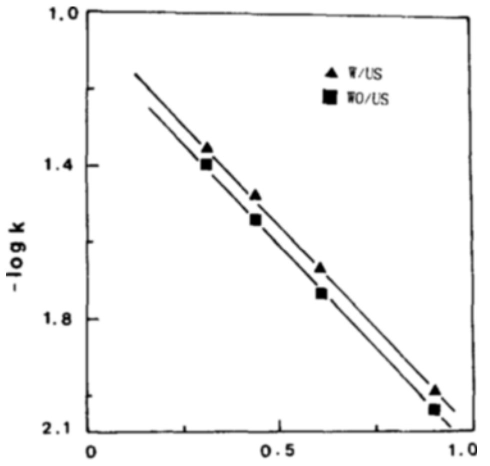


Fig. 10. The plot of log k vs. log $C_H{}^+$ for the maltose hydrolysis at 100°C and 3 wt% maltose.

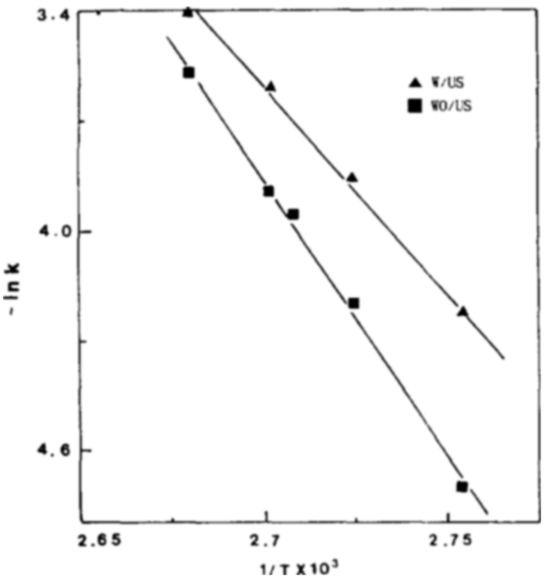


Fig. 11. The Arrhenius temperature dependence of the reaction rate constants of maltose hydrolysis (3 wt% maltose and 3 wt% H_2SO_4).

enhanced-degradation rate of polymer decreased to about 25 and 120% at 100 and 120℃, respectively, compared to at 80℃. So it is not unexpected that the relative enhancement is dependent on the temperature.

The activation energies were 23.4 and 30.2 Kcal/mole for the ultrasound-aided and for the control reaction, respectively, as shown at Fig. 11. The value of 30.2 Kcal/mole in the case of control reaction agrees well with the other work [12] for dextran hydrolysis. But the activation energy of ultrasound-aided reaction was much less than that of control reaction, which disagrees with Kristal et al. [12]. They reported that the activation energies were identical in both cases while the frequency factor was increased for ultrasound-aided reaction. Kristal et al. [12] carried out their experiment at lower temperature at which the ultrasound effects were fairly independent of the temperature. So it is very difficult to compare the two results exactly.

The proposed explanations for ultrasound effects are an increase in mixing effect, the rise in local temperature and pressure by the collapse of cavitation, the promotion of vibratory motion of the reacting molecules [10], and the facility of ionization of water. Among these many factors, the extreme temperature and pressure in the sonication bubbles and interfacial region being formed when the bubbles were collapsed seems to be the main factor. This result was expressed as the alleviation of activation energy in the case of ultrasound irradiation. The temperature dependence of the relative enhancements by ultrasound could be explained by the results of different activation energy. The larger enhancement by ultrasound at the lower temperature.

The complete expressions for rate constants by the experimental results were follows;

$$k^C = 3.714\times10^{16}\ C_H{}^+\ \exp(-15200/T)\ \text{and}$$
$$k^U = 4.539\times10^{12}\ C_H{}^+\ \exp(-11800/T).$$

CONCLUSION

Sulfuric acid-catalysed hydrolysis of starch was enhanced by ultrasound irradiation. And the relative enhancements were dependent on the temperature in the range of 90 and 100℃ and at a dilute acid of 1-5 wt%.

The model reaction of hydrolysis of glucosidic linkages showed that sulfuric acid catalysed hydrolysis of maltose were the first order respect to the maltose concentration and the H^+ concentration, respectively. The model reaction also showed that the relative enhancement depended on the temperature. And the ultrasound effects was expressed as the alleviation of activation energy in the case of ultrasound irradiation. This was believed due to the extreme rise of local temperature and pressure by the collapse of cavitation bubbles.

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REFERENCES

1. Mestres, C., Colonna, P. and Buleon, A.: *J. Food Science,* **53**(6), 1809 (1988).
2. Hughes, J. F.: US Patent 4,221,609 (1980).
3. Muller, W. C. and Miller, F. D.: US Patent 4,448, 881 (1984).
4. Assarsson, P. G. and Nagasuye, J. H.: US Patent 4,469,524 (1984).
5. Muller, W. C. and Miller, F. D.: US Patent 4,407, 955 (1983).
6. Muller, W. C. and Miller, F. D.: US Patent 4,421, 856 (1983).
7. Banks, W., Greenwood, C. T. and Muir, D. D.: *Die Stärke,* **25**(12), 405 (1973).
8. Faithfull, N. T.: *J. Sci. Food Agric.,* **50**, 419 (1990).
9. Muller, W. C. and Miller, F. D.: US Patent 4,266, 027 (1981).
10. Chen, J. W. and Kalback, W. M.: *I&EC Fundamentals,* **6**(2), 175 (1967).
11. Jarowenko, W.: "Encyclopedia of Chemical Technology", Vol. 12, pp. 787, edited by Mark, H. F., Othmer, D. F., Overberger, C. G. and Seaborg, G. T., Kirk-Othmer, A Wiley-Interscience Pub., John Wiley & Sons, NY., 1983.
12. Kristol, D. S., Khamis, A. A. and Parker, R. C.: *Ind. Eng. Chem. Prod. Res. Dev.,* **23**, 74 (1984).
13. Schuchardt, U., Joekes, I. and Duarrte, H. C.: *J. Chem. Tech. Biotechnol.,* **39**, 155 (1987).
14. Whistler, R. L.: "Starch: Chemistry and Technology", Vol. 1, pp. 1, edited by Whistler, R. L. and Paschell, E. F., Academic Press Inc., New York, 1965.
15. Nakamura, A. and Tsutsui, M.: "Principle and Applications of Homogeneous Catalysis", John Wiley & Sons, New York, 1980.
16. Cox, R. A. and Yates, K.: *J. Am. Chem. Soc.,* **100** (12), 3861 (1978).
17. Pethrick, R. A.: "Advances in Sonochemistry", Vol. 2, pp. 65, edited by Mason, T. J., JAI Press Ltd., 1991.