Research Article

Mass Transfer and Chemical Reaction Approach of the Kinetics of the Acetylation of *Gadung* Flour using Glacial Acetic Acid

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Abstract

Acetylation is one of the common methods of modifying starch properties by introducing acetil (CH$_3$CO) groups to starch molecules at low temperatures. While most acetylation is conducted using starch as anhidroglucose source and acetic anhydride or vinyl acetate as nucleophilic agents, this work employ reactants, namely flour and glacial acetic acid. The purpose of this work are to study the effect of pH reaction and GAA/GF mass ratio on the rate of acetylation reaction and to determine its rate constants. The acetylation of *gadung* flour with glacial acetic acid in the presence of sodium hydroxide as a homogenous catalyst was studied at ambient temperature with pH ranging from 8-10 and different mass ratio of acetic acid : *gadung* flour (1:3; 1:4; and 1:5). It was found that increasing pH, lead to increase the degree of substitution, while increasing GAA/GF mass ratio caused such decreases in the degree of substitution, due to the hydrolysis of the acetylated starch. The desired starch acetylation reaction is accompanied by undesirable hydrolysis reaction of the acetylated starch after 40-50 minutes reaction time. Investigation of kinetics of the reaction observed that the value of mass transfer rate constant (K_{cs}) is smaller than the surface reaction rate constant (k). Thus, it can be concluded that rate controlling step is mass transfer. © 2015 BCREC UNDIP. All rights reserved

Keywords: *gadung* flour; glacial acetic acid; acetylation; kinetics; degree of substitution

1. Introduction

Acetylated starch is a starch ester with the acetyl group introduced at low temperature [1]. Acetylated starches are used in a large variety of foods manufacturing including baked, canned pie fillings, sauces, retorted soups, frozen foods, baby foods, salad dressings, and snack foods [2]. Acetylated starches with degree of substitution (DS) between 0.01-0.2 are approved by the FDA for used as food materials [3]. Their usage is based on properties with respect to film forming, binding, adhesivity, thickening, stabilizing and texturing. Highly acetylated starches with a degree of substitution (DS) of 2 to 3 were of research interest from 1950 to 1980 for their solubility in acetone and chloroform and for their thermoplasticity [4, 5].

Acetylated starches are commercially produced by acetylation of starch with acetic

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anhydride, ketene, vinyl acetate, or a combination of these reagents [6]. Kinetic data on the acetylation of potato starch in a slurry system had been reported by Jetten *et al.* [7] and the rates of the acetylation reactions of potato starch using vinil acetate had been reported by de Graaf *et al.* [3]. However, no data have been published on the rates of the acetylation reactions of gadung flour (GF) with glacial acetic acid (GAA). As in all chemical reactions, acetylation depends upon factors such as reactant concentration, reaction time, pH, and the presence of catalyst [8], which finally determine the number of acetyl groups incorporated into the molecule. The purpose of this work are to study the effect of pH reaction and GAA/GF mass ratio on the rate of acetylation reaction and to determine its rate constants.

Acetylation is heterogeneous reaction which involving reactants of different phases, glacial acetic acid in the liquid phase and gadung flour in the solid phase (Figure 1). In general, heterogeneous reaction involves two processes, namely mass transfer (diffusion) and chemical reaction. Therefore, the overall reaction rate is a combination of these two processes. In acetylation reaction, there are two stages of reaction [9]: (i) diffusion of acetic acid from the bulk liquid to the surface of starch particles and (ii) reaction of acetic acid with starch at reaction surface.

2. Kinetic Modelling of Flour Acetylation

2.1. Diffusion of acetic acid from the bulk liquid to the surface of starch particles

In this reaction, the combined film assumption is imposed on the solid film region, due to the diffusion resistance of fluid through the solids film is greater than the resistance of fluid through the fluid film. The concentration gradient can be approximated as in Figure 2. The rate of mass transfer is

$$-\frac{dC_{Al}}{dt} = K_{cs}\frac{S_{pt}}{V_{pt}}(C_{As}* - C_{As}) \qquad (1)$$
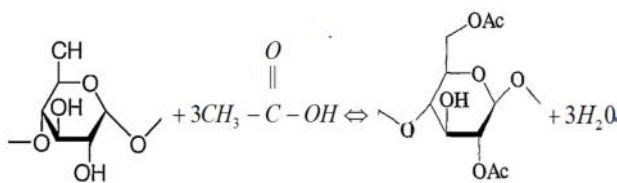
Figure 1. Starch acetylation reaction

with K_{cs} = combined mass transfer coefficient in the solid phase. In this case, $C_{As}*$ equilibrium with C_{Al}, thus:

$$C_{As}* = H \times C_{Al} \qquad (2)$$

Substitution Equation (2) to Equation (1), gives:

$$-\frac{dC_{Al}}{dt} = K_{cs}\frac{S_{pt}}{V_{pt}}(HC_{Al} - C_{As}) \qquad (3)$$

2.2. Reaction of acetic acid with starch at reaction surface

Theortically, three free hydroxyl (OH) groups on C2, C3 and C6 of the anhydroglucose unit of the starch molecule were replaced with acetyl groups during acetylation (Figure 1). Thus, the rate of acetic acid decomposition:

$$-r_{At} = -\frac{dC_{Al}}{dt} = k\frac{S_{pt}}{V_{pt}}C_{Ag}^m C_{As}^n \qquad (4)$$

From previous studies of the acetylation of potato starch with vinyl acetate, de Graaf *et al.* [3] reported that acetylation reaction was first order both in starch and acetyl.

$$-\frac{dC_{Al}}{dt} = k\frac{S_{pt}}{V_{pt}}C_{Ag}C_{As} \qquad (5)$$

2.3. Hydrolysis of starch acetate

The starch acetylation reaction can be accompanied by hydrolysis reaction of the acetylated starch (Figure 2). The rate of starch acetate hydrolysis:

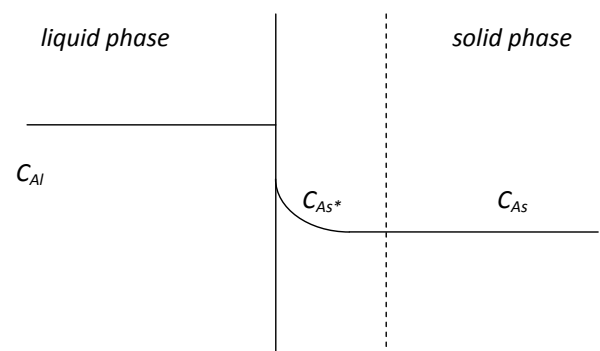$$-\frac{dC_{RA_c}}{dt} = 3\frac{dC_{Al}}{dt} = k_h\frac{S_{RA_c}}{V_{RA_c}}C_{RA_c}^m C_{H_2O}^n \qquad (6)$$

Figure 2. Mass transfer between phases in the combined films

$$\frac{dC_{Al}}{dt} = \frac{1}{3}k_h \frac{S_{RA_c}}{V_{RA_c}} C_{RA_c}^m C_{H_2O}^n$$

(7)

Based on the starch acetate SEM analysis [10], it has been proven that the granula size of the acetylated starch is larger than the native one, thus it can be formulated that $S_{RAc} = a\, S_{pt}$ and $V_{RAc} = b\, V_{pt}$, where a and b are multiple value of anhidroglucose surface area and volume.

$$\frac{dC_{Al}}{dt} = \frac{1}{3}k_h \frac{aS_{pt}}{bV_{pt}} C_{RA_c}^m C_{H_2O}^n$$

(8)

From previous studies, starch acetate hydrolysis reaction is known to be first- order in both R_{Ac} and OH^- [3], thus:

$$\frac{dC_{Al}}{dt} = \frac{1}{3}k_h c \frac{S_{pt}}{V_{pt}} C_{RA_c} C_{H_2O}$$

(9)

in this study, the concentration of water (C_{H2O}) are in excess, so the changes in its concentration are negligible, thus Equation (9) becomes:

$$\frac{dC_{Al}}{dt} = \frac{1}{3}k_h c \frac{S_{pt}}{V_{pt}} C_{RA_c}$$

(10)

based on stoichiometric equations,

$$C_{RA_c} = \frac{x}{3} C_{Alo}$$

Equation (10) may be written as:

$$\frac{dC_{Al}}{dt} = \frac{1}{9}k_h cx \frac{S_{pt}}{V_{pt}} C_{Alo}$$

(11)

The forward reaction rate (starch acetate formation) is a function of C_{Ag} and C_{Al}, and the reverse reaction rate (starch acetate hydrolysis) is a function of C_{RAc} and water. The overall reaction rate of starch acetylation hydrolysis are given by:

The diffusion equation for mass transfer:

$$-\frac{dC_{Al}}{dt} = K_{cs} \frac{S_{pt}}{V_{pt}} (HC_{A_l} - C_{A_s})$$

(3)

The equation for surface reaction:

$$-\frac{dC_{Al}}{dt} = k \frac{S_{pt}}{V_{pt}} C_{A_g} C_{A_s}$$

(5)

The hydrolisis rate equation:

$$\frac{dC_{Al}}{dt} = \frac{1}{9}k_h c \frac{S_{pt}}{V_{pt}} x C_{Alo}$$

(11)

The overall reaction rate equation:

$$-\frac{dC_{Al}}{dt} = k''' \left(H \frac{S_{pt}}{V_{pt}} C_{Al} - \frac{cxS_{pt}}{9V_{pt}} \right)$$

(12)

where k'' is the overall reaction rate constant:

$$\frac{1}{k'''} = \frac{1}{k_h C_{Alo}} + \frac{1}{K_{cs}} + \frac{1}{kC_{Ag}}$$

(13)

Equation (10) is described as follows:

$$-\frac{dC_{Al}}{dt} = k''' \left(H \frac{4\pi R^2}{\frac{4}{3}\pi R^3} C_{Al} - \frac{cx 4\pi R^2}{9 \times \frac{4}{3}\pi R^3} \right)$$

$$-\frac{dC_{Al}}{dt} = k''' \frac{1}{R} \left(3HC_{Al} - \frac{cx}{3} \right)$$

(14)

where R is radius of anhidroglucose particle at time t (which is an unknown quantity). This can be eliminated with the help of mass of anhidroglucose and fractional conversion of anhidroglucose.

The mass of anhidroglucose is given by:

$$w = volume \times density$$

$$w = \frac{4}{3}\pi \times R^3 \times \rho \times Z$$

(15)

where Z is the number of anhidroglucose molecules.

Based on the starch acetate SEM analysis [10], it has been proven that the granula size of the acetylated starch is larger than the native one, thus, the fractional conversion of anhidroglucose in terms of weight of anhidroglucose is:

$$x = \frac{(w_t - w_{in})}{w_{in}}$$

$$x = \frac{(R^3 - R^3{}_{in})}{R^3{}_{in}}$$

(16)

From Equation (16) the radius of anhidroglucose molecule at time t is:

$$R = R_{in}\left(1 + x\right)^{1/3}$$

(17)

Substitution Equation (17) to Equation (14), gives:

$$-\frac{dC_{Al}}{dt} = k'''\frac{1}{R_{in}\left(1+x\right)^{1/3}}\left(3HC_{Al} - \frac{cx}{3}\right)$$

(18)

3. Materials and Methods

3.1. Materials

Native gadung flour used in this work was obtained from milling and sieving of treated gadung tuber chips using a method suggested by Kumoro et al. [11] and Kumoro et al. [12]. Glacial acetic acid and other chemicals used in this work were of analytical grade (≥99.90 % w/w) were purchased from Sigma-Aldrich Pte. Ltd. (Singapore) and directly used without further purification.

3.2. Apparatus

The acetylation of gadung flour study in this work employed mainly a 500 ml capacity beaker glass and a hot plate magnetic stirrer.

3.3. Procedure

The acetylation was carried out by dispersing 20 g of gadung flour in 100 ml distilled water to obtain gadung flour slurry with 20% consistency. The pH of the slurry obtain was adjusted to a certain value (8, 9 or 10) using 1 M NaOH. To facilitate flour dispersion, the slurry was stirred magnetically for 30 minutes. Then, a predetermined mass of glacial acetic acid was added slowly to the reaction mixture while maintaining a pH to a certain value (8, 9 or 10). The acetylation reaction proceeded for 10 to 60 minutes before being terminated by bringing the pH to 5.5 by addition of 1 M HCl. The acetylated flours were obtained by filtration of the reaction mixture and followed by threefold washing of the flours using distilled water with 1:3 (w/v). The acetylated flours were then dried in an electric oven at 50 ºC till dryness before subjected to degree of substitution analysis.

3.4. Analyses

The degree of substitution (DS) and residual acetic acid concentration (C_{Al}) were determined titrimetrically, following the method of Sodhi and Singh [13]. Acetylated starch (1.0 g) was placed in a 250 ml flask and 50 ml of 75 ml/100 ml ethanol in distilled water were added. The loosely stopper flask was agitated, warmed to 50 ºC for 30 min, cooled and 40 ml of 0.5 M KOH were added. The excess alkali was back-titrated with 0.5 M HCl using phenolphthalein as an indicator. A blank, using the original unmodified starch, was also used. Degree of substitution is defined as the average number of sites per glucose unit that possess a substituent group [8].

$$\%Acetyl = \frac{(Vo - Vn) \times MHCl \times 0,043 \times 100}{M}$$

(19)

$$DS = \frac{162 \times \%\ Acetyl}{4300 - (42 \times \%\ Acetyl)}$$

(20)

Residual acetic acid concentration:

$$C_{Al} = \frac{(Vo - Vn) \times MHCl}{V}$$

(21)

Fractional conversion of acetic acid:

$$x = \frac{C_{Alo} - C_{Al}}{C_{Alo}}$$

(22)

4. Results and Discussion

4.1. Effect of the glacial acetic acid/gadung flour

To study the effect of the GAA/GF mass ratio to the degree substitution of acetylated gadung flour, acetylation reaction are run at ambient temperature and pH 8. The results are presented in Figure 4. From the calculation of degree of substitution, the concentration of residual acetic acid in the bulk liquid (C_{Al}) and the fractional conversion of acetic acid (x) can also be calculated. These value were put into Equation (12) and optimized using the solver program in Microsoft Excel 2007. In this study, the concentration of anhidroglucose (C_{Ag}) and glacial acetic acid at time t=0 (C_{Al}) are 0.0034
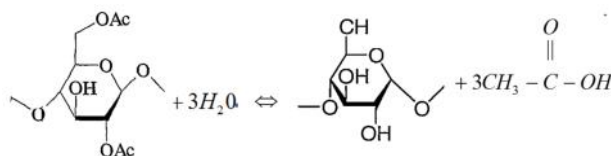

Figure 3. Starch acetate hydrolysis

mol g^{-1} and 1.2093 mol l^{-1}. The optimized values of kinetics parameters are presented in the Table 1. The kinetic parameters given in Table 1, then were substituted into equation (12) for the simulations. The experimental and calculated acetic acid concentrations in the bulk liquid are shown in Figure 5.

It can be seen that the higher concentration of acetic acid, the higher residual acetic acid in the liquid phase. In this study, the residual acetic acid in the liquid phase decrease with the increasing reaction time, until a certain time period (40-50 minutes). The longer the reaction time, the more time is available for an acetyl group to diffuse and undergo adsorption to the surface of starch molecules [14]. The desired starch acetylation reaction is accompanied by hydrolysis reaction of the acetylated starch after 40-50 minutes acetylation, which is indicated by the decreasing value of degree of substitution and the increasing concentration of residual acetic acid in the bulk liquid. Luo and Zhou [15] reported that the lower the concentration of acetyl groups in the starch acetate with increasing reaction time is caused by hydrolysis of the ester starch (starch acetate) produced or

elimination reactions as a result of excess water (from starch and byproducts esterification) are not discharged from the reactor during the reaction. Table 1 shows that the value of mass transfer rate constant (K_{cs}) is smaller than chemical reaction constant (k). Thus, it can be concluded that rate controlling step is mass transfer.

Figure 5 shows a comparison between the experimental data and the modeling results. Both graphs coincide each other, thus the optimized value of mass transfer rate constant (K_{cs}), chemical reaction constant (k), and hydrolysis reaction rate constants (k_h) are considered quite valid to represent the experimental data.

4.2. Effect of pH

To study the effect of pH reaction to the degree substitution of acetylated *gadung* flour, acetylation reaction were run at ambient temperature and GAA/GF mass ratio 1:3. The results are presented in Figure 6. From the calculation of degree of substitution, the concentration of residual acetic acid in the bulk liquid (C_{Al}) and the fractional conversion of

Table 1. Optimized kinetic parameters for acetylation of *gadung* flour at various mass ratio (GAA/GF)

Variable	DS	x (%)	k_h (g mol^{-1} m min^{-1})	k (g^2 mol^{-1} l^{-1} m min^{-1})	K_{cs} (g l^{-1} m min^{-1})
GAA/GF 1:3	0.049	0.231	5.37E-13	3.59E-06	1.25E-08
GAA/GF 1:4	0.060	0.371	6.05E-13	3.61E-06	1.26E-08
GAA/GF 1:5	0.115	0.343	4.90E-13	3.71E-06	1.29E-08
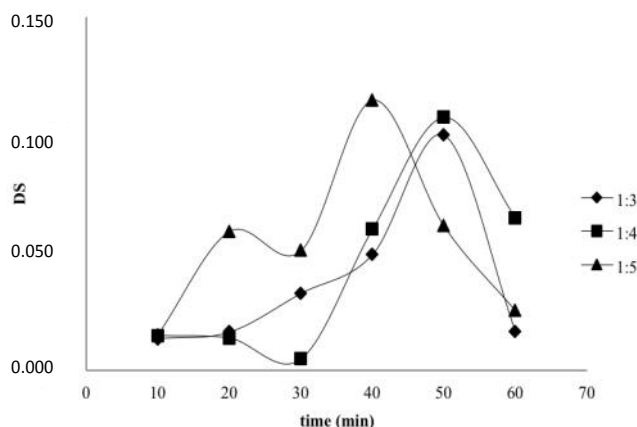
Figure 4. Degree of substitution vs time for various mass ratio (GAA/GF) (pH 8 at 30 °C)
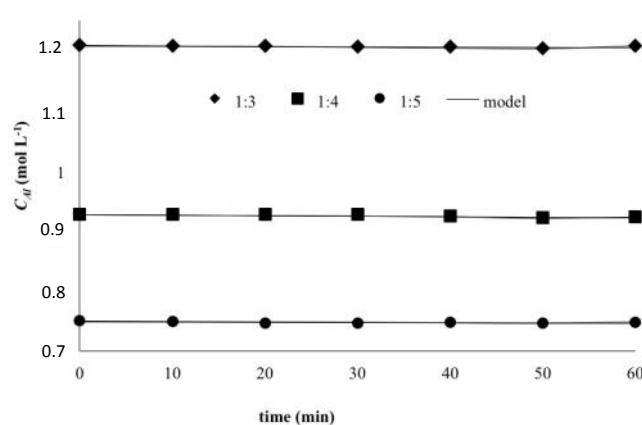
Figure 5. Experimental and simulated glacial acetic acid concentration change in the bulk liquid (pH 8; at 30 °C)

acetic acid (*x*) can also be calculated. These value were put into Equation (12) and optimized using the solver program in Microsoft Excel 2007. In this study, the concentration of anhidroglucose (C_{Ag}) and glacial acetic acid at time *t*=0 (C_{Al}) are 0.0034 mol g-1 and 1.2093 mol l-1. The optimized values of kinetics parameters are presented in the Table 2. The kinetic parameters given in Table 2, then were put into Equation (12) for the simulations. The experimental and calculated acetic acid concentrations in the bulk liquid are shown in Figure 7.

It can be seen that the residual concentration of acetic acid in the liquid phase decreased with increasing pH of the reaction. The higher the pH, means the more NaOH was added. Sodium hydroxide in the acetylation reaction acts as a reaction initiator to form the alcoholate ions along the starch polymer which can activate the hydroxyl groups on the starch [16] and lead to a nucleophilic attack on acetic acid [17]. Sodium hydroxide also acts as a catalyst which can affect the swelling of the starch molecules, thereby increasing the ability of molecular diffusion around starch acetate [18]. This causes the concentration of residual acetic acid in the liquid phase decreased with increasing pH of the reaction.
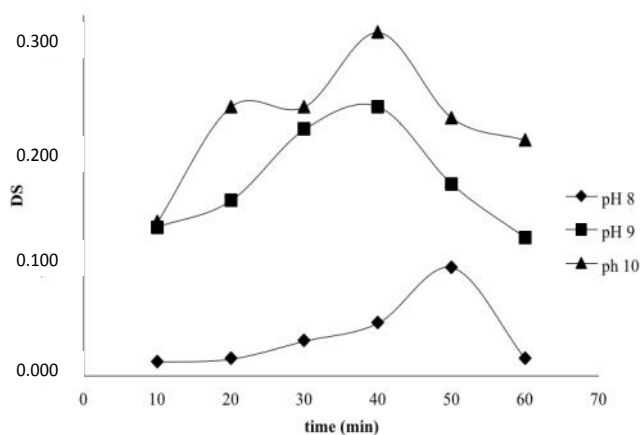
The desired starch acetylation reaction is accompanied by hydrolysis reaction of the acetylated starch after 40 minutes (pH 9 and 10) and 50 minutes (pH 8) acetylation, which characterized by the decreasing value of degree of substitution and the increasing concentration of residual acetic acid in the bulk liquid. Song *et al.* [19] reported that at pH 9.5, side reaction (acetate starch hydrolysis) will be the dominant reaction. Luo and Zhou [15] reported that the lower value of acetyl groups concentration in the starch acetate with increasing reaction time is mainly caused by hydrolysis of the starch ester (starch acetate). This hydrolysis reaction is likely to happen due to excess water in the system, which comes from moisture of the starch and byproducts esterification.

The value of hydrolysis reaction rate constants (k_h) at pH 9 and 10 are greater than pH 8. This finding is consistent with that reported by Song *et al.* [19] who reported that at pH 9.5, side reaction (acetate starch hydrolysis) will be the dominant reaction. The optimized values of the reaction rate constants presented in Table 2 show that the value of mass transfer rate constant (K_{cs}) is smaller than chemical reaction constant (*k*). Thus, it can be concluded that rate controlling step is mass transfer.
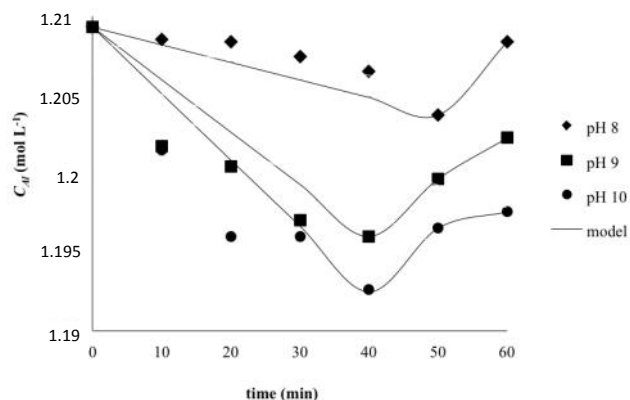

Figure 6. Degree of substitution vs time for various pH (GAA/GF = 1:3 at 30 ºC)

Figure 7. Experimental and simulated glacial acetic acid concentration change in the bulk liquid (GAA/GF = 1:3 at 30 ºC)

Table 2. Optimized kinetic parameters for acetylation of *gadung* flour at various pH

Variable	DS	x (%)	k_h (g mol-1 m min-1)	k (g2 mol-1 l-1 m min-1)	K_{cs} (g l-1 m min-1)
pH 8	0.049	0.231	5.37E-13	3.59E-06	1.25E-08
pH 9	0.246	1.098	7.96E-12	1.08E-05	3.75E-08
pH 10	0.314	1.378	8.00E-12	1.37E-05	4.75E-08

Figure 7 shows a comparison between the experimental data and the modeling results. Both the graph show coincide each other, thus the value of mass transfer rate constant (K_{cs}), chemical reaction constant (k), and hydrolysis reaction rate constants (k_h) are considered quite valid to represent the experimental data.

5. Conclusion

The reaction kinetics of acetylation of GF with GAA catalyzed by NaOH has been determined. The degree substitution increases with increasing pH, while increasing ratio of acetic acid : gadung flour, decreases the degree of substitution, that is due to the acetate starch hydrolysis. The desired starch acetylation reaction is accompanied by hydrolysis reaction of the acetylated starch after 40-50 minutes acetylation. Investigation of kinetics of the reaction indicated that the value of mass transfer rate constant (K_{cs}) is smaller than the chemical reaction constant (k). Thus, it can be concluded that rate controlling step is mass transfer.

Acknowledgments

Nomenclatures

GAA   Glacial acetic acid
GF   *Gadung* flour
dC_{Al}/dt Rate of decomposition acetic acid (mmol ml^{-1} min^{-1})
dC_{pt}/dt Rate of decomposition anhidroglucose (mol g^{-1} min^{-1})
C_{Al} Concentration of acetic acid in the bulk liquid at time t (mol l^{-1})
C_{Al} Concentration of acetic acid in the bulk liquid at time $t=0$ (mol l^{-1})
C_{As} Concentration of acetic acid at the surface of the anhydroglucose (mol g^{-1})
C_{As}^* Concentration of acetic acid at the layer film (mol g^{-1})
C_{Ag} Concentration anhidroglucose at time t (mol g^{-1})
C_{H2O} Concentration of water in the bulk liquid at time t (mol l^{-1})
t Time (min)
H Henry's Law Constant (g l^{-1})
S_{pt} Surface area of anhidroglucose (m^2)
S_{RAc} Surface area of starch acetate (m^2)

V_{pt} Volume of anhidroglucose (m^3)
V_{RAc} Volume of starch acetate (m^3)
a multiple value of anhidroglucose surface area
b multiple value of anhidroglucose volume
c a/b
k Surface reaction rate constant (g^2 mol^{-1} l^{-1} m min^{-1})
K_{cs} Mass transfer coefficient in solid phase (g l^{-1} m min^{-1})
k_h Hydrolysis reaction rate constant (gmol^{-1} m min^{-1})
k'' Overall reaction rate constant (g l^{-1} m min^{-1})
x Fractional conversion of acetic acid at time t
w Mass of anhidroglucose (g)
w_{in} Initial mass of anhidroglucose (g)
w_t Mass of anhidroglucose at time t (g)
R The radius of the starch surface (m)

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